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The minutes of the previous meeting were read, and were confirmed and signed as a correct record.

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A brief history is given of the development of synthetic lubricants for aircraft gas turbines in Great Britain and in the U.S.A., with a discussion of the methods of test used in their evaluation.

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Synthetic lubricants were in regular use in jet aircraft in the U.K. and in the U.S.A. in 1952, since which time the demand for them has been increasing quite rapidly, and mineral oils have been to a large extent, though not entirely, superseded. As pointed out by Davidson, Cooley, and Way,[2] mineral oils gave excellent service in the earlier gas turbine engines, but, as performances were gradually increased, troubles were experienced due to coking, high evaporation loss, and inadequate load-carrying capacity, the latter being particularly important in the case of turbo-prop engines.

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Engine	Type	Great Britain and Ireland	Rest of Europe
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Bristol-Siddeley Proteus	Turbo-prop	136	—
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All these engines except the last two have been designed to operate on oils of viscosity not less than 7·5 cS at 210° F, although the Avon and Conway engines can also run on the low viscosity oils (3 cS minimum at 210° F) normally used in the U.S.A.

* MS received 2 June 1960.

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Both in the U.K. and in the U.S.A. synthetic oils have been developed which will lubricate either turbo-jet or turbo-prop engines equally satisfactorily.

While turbo-jet engines require to have a comparatively small quantity of oil in circulation, turbo-prop engines need considerably more to provide lubrication of the reduction gear and cope with the heat transfer problems. Thus the Tyne, a typical example of a high-powered turbo-prop engine, requires as much as 110 pints of oil, whereas the Avon, a typical turbo-jet engine, needs only 12 pints. Oil consumption is generally quite low, but drain periods vary greatly, from about 200 hours in some engines to around 2000 hours in others, in which latter case they are commensurate with engine overhaul life.

The life of an oil in an engine will obviously depend upon both the nature and the performance of the oil and upon engine design and operating conditions. In this latter connexion, the bulk oil temperature and the temperature of the hottest bearing are especially important, as well as the degree of aeration of the lubricant.

In civil aircraft engines an oil may be considered to give satisfactory performance if it is not the limiting factor in engine overhaul life. In military engines the position is somewhat different, since these engines are liable to be operated under much more severe conditions for much shorter periods, following which the oil will be drained and the engine overhauled. The ideal oil must therefore perform satisfactorily under both sets of conditions, *i.e.* it must not be unduly volatile, it must carry the load on the reduction gearing in turbo-prop engines, and, above all, it must not form coke in the hot bearings.

Continual efforts are being made to increase engine performance, with a consequent stepping up of bulk oil and bearing temperatures, so that the search for improved lubricants goes on with unremitting energy.

In this paper an attempt is made to trace briefly the development of existing lubricants and test methods and to indicate future trends in this field.

SYNTHETIC BASE FLUIDS

A synthetic gas turbine lubricant consists essentially of a liquid organic compound or mixture of compounds and one or more antioxidants. Other additives may also be present, *e.g.* load-carrying additives, corrosion inhibitors, metal deactivators, and foam inhibitors.

The essential requirements of a synthetic base fluid are:

(1) It must remain stable and fluid over a wide range of temperatures.

(2) It must have low volatility at high temperatures.

(3) It must be a good lubricant.

(4) It must, when combined with suitable antioxidants, have good resistance to oxidation at high temperatures and be non-corrosive to the metals present in the engine.

(5) It must be substantially non-foaming.

All the current synthetic lubricants are based on carboxylic acid esters, but other types of fluid have been considered, *e.g.* silicones, silicone/diester blends, silicates, and polyglycol ethers. Certain branched-chain diesters of dicarboxylic acids have proved to be ideally suited for use as base fluids in this connexion.

Esters of this general type were extensively studied during the second world war in Germany by Zorn [3] and concurrently in the U.S.A. at the Naval Research Laboratory, Washington, D.C. The German work has been reviewed by Tingle [4] and Horne,[5] whilst the American work has been described by Bried and co-workers [6] and Atkins and co-workers.[7]

At this time interest was centred principally in lubricants for aircraft instruments which would remain liquid at extremely low temperatures. When the demand came for synthetic lubricants for gas turbine engines the exceptional viscosity–temperature properties and low volatility of certain of these esters immediately suggested the possibility of their use in this connexion, and a large volume of work was carried out with a view to selecting the most suitable esters and evaluating suitable antioxidants for them. Surveys of this work have been given by Cohen and co-workers [8] and by McTurk,[9] who has tabulated physical test data on over 800 esters.

The general conclusions arising from this work may be summarized thus:

(1) The higher the molecular weight, the lower the volatility of the ester.

(2) The longer the " backbone," the better the viscosity–temperature properties and the higher the viscosity.

(3) Branched chains are necessary to ensure that the ester remains liquid at low temperatures.

The effect of structure on physical properties has been discussed by Murphy and Zisman [10] in relation to a variety of synthetic lubricants.

Branched-chain higher alcohol esters of sebacic acid possess the optimum properties in these respects, and esters such as di-(2-ethyl hexyl) sebacate (dioctyl sebacate) and di-(3,5,5-trimethyl hexyl) sebacate (dinonyl sebacate) have been used as the basis for most of the synthetic oils on the market, although in the U.S.A. certain compositions have been used based on azelate esters, *e.g.* di-*iso*-octyl azelate, which have the advantage of being somewhat less costly.

These simple diesters have viscosities around 3 cS at 210° F, and are thus suitable base fluids for the low viscosity oils demanded in the U.S.A. In order to meet the British requirements, however, various complex esters have been synthesized which, when blended with the diesters, provide lubricants of the

correct viscosity (7·5 cS at 210° F). A large number of these complex esters have been described by McTurk [9] and in a voluminous patent literature,[11] the most satisfactory type of ester being derived from a polyethylene glycol, sebacic or azelaic acid, and a branched-chain alcohol.

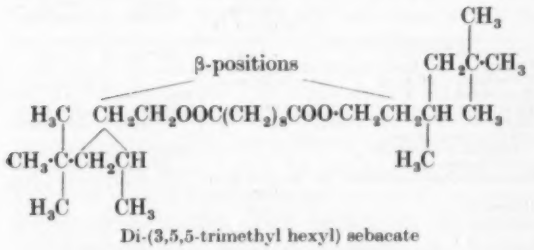
Before leaving the subject of esters some reference should be made to the so-called " hindered " esters, which are characterized by the possession of a neopentyl grouping, with no hydrogen atoms on the carbon atom in the β-position to the ester group. Esters of this type derived from trimethylolethane were among those studied in Germany during the war,[4] whilst others have been synthesized and examined by McTurk [9] and by Fainman and Barnes.[12] These include esters derived from the commercially available polyhydric alcohols trimethylolpropane and pentaerythritol.

It has been postulated by Sommers and Crowell [13] that diesters such as dioctyl sebacate decompose thermally to form acids and 1-alkenes by a mechanism involving the removal of hydrogen from the β-carbon atom. When β-hydrogen is absent this reaction cannot take place, and decomposition can occur only by a free radical mechanism.

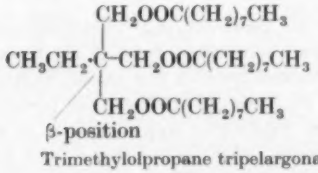
The " hindered " esters thus possess considerably greater thermal stability than the conventional diesters.

In fact, Fainman and Barnes [12] found that a branched-chain di-octyl azelate decomposed almost three times as fast at 500° F as esters derived from trimethylolpropane and pentaerythritol.

The difference in structure between the conventional diesters and the " hindered " esters may best be seen by considering the formulæ of typical members of each series, namely, di-(3,5,5-trimethyl hexyl) sebacate and trimethylolpropane tripelargonate—



Di-(3,5,5-trimethyl hexyl) sebacate



Trimethylolpropane tripelargonate

Although the " hindered " esters possess greater thermal stability than the conventional diesters, their viscosity indices are lower. A comparison between the physical properties of these esters is made in Table II.

TABLE II

Physical Properties of Esters

	Di-(3,5,5-trimethyl hexyl) sebacate	Trimethylolpropane tripelargonate
Viscosity at 210° F, cS	4·66	4·62
Viscosity at 100° F, cS	19·3	22·9
Viscosity at −40° F, cS	3540	6000 approx
Viscosity Index	180	135
ASTM slope	0·65	0·71
Pour point, ° F	−10	−55
Flash point, ° F	430	525

A further advance in the field of " hindered " esters has been made by Durr and Thompson,[14] who have prepared esters having improved thermal and oxidation stability from alcohols having the neopentyl structure and ααα′α′-tetraethylazelaic acid.

Although the conventional diester-based lubricants are likely to provide satisfactory lubrication of the great majority of aircraft gas turbine engines for some time to come, lubricants based on " hindered " esters are likely to be required for supersonic aircraft with speeds up to about Mach 2·5. For speeds in excess of this, however, it would seem that one must look away from esters altogether to materials having a more chemically stable structure, even though this may mean sacrificing other desirable properties.

In this connexion it may be as well to review some of the types of material which at various times have been considered as possible base fluids for gas turbine lubrication.

Silicones have been fairly extensively studied. Their exceptional viscosity–temperature properties coupled with good oxidation stability are well known. Their lubricating properties, however, are notoriously poor, and very high wear can be experienced when these substances are used to lubricate steel rubbing surfaces. They are also prone to cause foaming problems. The performance of silicones and their limitations have been discussed by several authors.[15–17]

Blends of silicones and diesters were shown by Johnson, Swikert, and Bisson [15] to have better lubricating properties than either silicones or diesters used alone. Engine experience has not proved satisfactory, however;[2] in fact, it is known that one such blend, tested in an engine, led to disastrous results.

Silicate esters have better lubricating properties than silicones,[15, 18] but suffer from inadequate high temperature oxidation and hydrolytic stability. They are widely used as hydraulic fluids, but have not been found satisfactory as engine lubricants. Special silicate esters of improved hydrolytic stability have been synthesized by Miller and co-workers.[19]

Polyglycol ethers have also been considered by several workers.[2, 15, 18] They are excellent lubricants with reasonably good viscosity–temperature characteristics and have the advantage that they form volatile degradation products and leave no solid residues. Those compounds which are sufficiently low in viscosity to be used as gas turbine lubricants are, however, too volatile,[18] whilst, as a class, the polyglycol ethers are somewhat more susceptible to oxidative and thermal breakdown than the diesters.

In spite of these apparent disadvantages, which evidently deterred earlier workers from pursuing the investigation of these materials, the authors have found it possible to use certain higher polyglycol ethers as thickeners for diester-based lubricants with very satisfactory results. In this connexion the selection of the compound is of particular importance, as is the choice of antioxidant to stabilize the blend. Lubricants may be prepared in this way having excellent shear and thermal stability, comparable to that exhibited by the diester/complex ester blends to which reference has already been made.

Other synthetic materials which have received some consideration include phosphate esters,[18] phosphonates,[15] and certain special types of compound which will be considered in a later section dealing with higher temperature lubricants.

DEVELOPMENTS IN THE U.K. AND IN THE U.S.A.

The maximum viscosity of a lubricant that will permit easy starting of an engine from cold has been estimated as being somewhere in the range 5000–20,000 cS.[20] The minimum temperature likely to be reached by grounded aircraft operating from the U.K. has been considered to be −40° F, but in the U.S.A. this minimum temperature has been estimated at −65° F.

This difference in low temperature requirement between the two countries has resulted in the development of lubricants along different lines. Thus, in the U.S.A., lubricants have been compounded based upon simple diesters, such as dioctyl sebacate, with antioxidant and load-carrying additives, these lubricants having viscosities of 3–4 cS at 210° F, whereas in the U.K. the less stringent low temperature requirement has permitted the development of more viscous oils. These latter so-called "7·5 cS oils" have advantages over the "3 cS oils" with respect to volatility and load-carrying ability, and in minimizing bearing fatigue failures, which latter are believed to be a function purely of the viscosity of the lubricant.[16]

The advantages of the "7·5 cS oils" over the "3 cS oils" are perhaps greater with reference to turbo-prop engines, but the natural desire to have one oil specification covering both types of engines has led to concentration in the U.K. on the former and in the U.S.A. on the latter. The British Ministry of Aviation, although at one time willing to consider the use of 5 cS oils, have never felt able to accept 3 cS oils for military purposes, partly because the propeller-control units in many British turbo-props have been designed to operate on 7·5 cS oils. On the other hand the U.S. military authorities have never been prepared to relax their low-temperature requirements and have been able to lubricate all their engines satisfactorily on 3 cS oils.

The British military requirements for synthetic gas turbine lubricants are covered by Ministry of Aviation Specification D.Eng. R.D. 2487, of which there have been three issues dated 1952, 1954, and 1957, with a fourth pending, while the U.S. military requirements are covered by U.S. Military Specification MIL-L-7808, of which there have also been four issues, the latest, MIL-L-7808D, being in 1959.

In addition, some of the engine manufacturers have their own specifications. Thus, Rolls-Royce Ltd, while adhering to the general physical requirements of D.Eng. R.D. 2487, apply certain additional laboratory oxidation and corrosion tests, which will be discussed more fully in a later section. Pratt & Whitney Aircraft in the U.S.A. also have their own specification for 3 cS oils, while one U.S. engine manufacturer, the Allison division of General Motors, actually specify a 7·5 cS oil for their turbo-prop engines.

The physical test requirements of D.Eng. R.D. 2487 (Issue No. 3), MIL-L-7808D, and Allison EMS-35G specifications are listed in Table III.

TABLE III

Synthetic Lubricant Specifications—Physical Tests

	D.Eng. R.D. 2487 (Issue No. 3)	MIL-L-7808D	Allison EMS-35G
Viscosity at 210° F, cS	7·5 min	3·0 min	7·5 min
Viscosity at 100° F, cS	39·0 max	11·0 min	—
Viscosity at −40° F, cS	13,000 max	—	13,000 max
Viscosity at −65° F, cS	—	13,000 max	—
Flash point, ° F	420 min	400 min	425 min
Pour point, ° F	—	−75 max	−60 max
Foaming (max values):			
Sequence 1-2-3 vol, ml	—	100-25-100	100-25-100
Collapse time, min	—	5-3-5	5-3-5
Evaporation loss (6½ hr at 400° F)	To be reported (at 392° F)	35% max	To be reported
Mineral acidity	Nil	—	—

In addition to load-carrying, oxidation/corrosion, engine tests, and sometimes bearing rig tests, all of which are discussed later in the paper, D.Eng. R.D. 2487 requires that the oil shall remain homogeneous and compatible with other approved oils at all temperatures between −54° and +280° C, the test procedure being specified. There is also a viscosity stability test, in which the viscosity at −40° F is repeated after the oil has been held at −65° F for at least 12 hours, a shear stability test, and a thermal

stability test. The shear stability test involves running the oil for 168 hours in an aircraft hydraulic pump, the viscosity at 100° F not to change by more than 5 per cent. The thermal stability test involves heating the oil for four 6-hour periods at 280° C under nitrogen, the viscosity change at 100° F not to exceed the limits −10 to +20 per cent. In the final issue of D.Eng. R.D. 2487, the shear stability test is being replaced by a simpler test using a diesel fuel injector.

These last two tests were introduced into Issue No. 3 because certain experimental lubricants, otherwise meeting the requirements of the specification, suffered a substantial drop in viscosity after testing in highly stressed turbo-prop engines or reduction gear rigs. An endurance test on the IAE Gear Machine, which was required in Issue No. 2, did not provide an adequate measure of shear stability. The polymethyacrylate thickening agents described by Glavis[21] suffer degradation due to shearing stresses into polymers of lower molecular weight, whilst at high temperatures the polymers " unzipper " down their whole length by splitting off monomer. Both of these processes result in a drop in viscosity. Polyester thickeners, though in general more shear stable, are also prone to thermal breakdown. Blends of diesters and complex esters or diesters and polyglycol ethers may be prepared free from both these defects.

Additional tests required by MIL-L-7808D specification include a viscosity stability test at −65° F, a rubber swell test, compatibility and storage stability tests. This last test, which was not required by MIL-L-7808C specification, is carried out by heating gallon cans of the oil in an oven at 180° F and performing lead corrosion tests on samples drawn at seven-day intervals. The lead corrosion value must not exceed 25 mg/in² after 14 days or 150 mg/in² after 45 days. Work at the Wright Air Development Centre has shown that this test correlates well with long-term storage tests at ambient temperature.

In the U.K. the situation has been that, as only one satisfactory lubricant was available in 1952, D.Eng. R.D. 2487 specification was written round it. Experimental oils submitted for approval against this specification have been tested by comparison with this approved oil and not merely against the stated specification requirements. The specification has always been worded so as to permit of engine tests and bearing rig tests being carried out at the discretion of the Ministry of Aviation, and it is quite understandable that the latter, having obtained an oil which gave satisfactory performance in service, should endeavour to ensure that any new oils which came up for evaluation should not be significantly inferior.

The development of alternative oils has not been an easy matter, owing to the necessity for carrying out tests in a variety of both turbo-jet and turbo-prop engines, some operating under very severe conditions.

The development of oils for use in civil aircraft has been somewhat less difficult, partly due to the less stringent operating conditions and partly due to the fact that Rolls-Royce Ltd some time ago devised a comprehensive series of laboratory tests from which engine performance could be predicted relatively simply and with a considerable degree of reliability.

In the U.S.A. the situation has been rather different. Since the simple diesters, such as dioctyl sebacate, met the viscosity requirements of MIL-L-7808, one of the chief problems that has beset chemists in the U.K., that of providing a thickening agent stable to high temperatures and to shearing stress, did not exist. Furthermore, oils have been approved to MIL-L-7808 provided that they met the specific test requirements set out in that specification, only one engine test, in a turbo-jet engine, being carried out. This over-simplified qualification procedure has led to difficulties, however, and some originally approved oils have since had their approvals withdrawn.

The specific requirements of the turbo-prop engine have been discussed by Christensen,[22] who has described work carried out at Wright Air Development Centre. It was concluded that the necessary degree of oxidation resistance could be obtained by incorporating a small amount of phenothiazine, whilst the necessary degree of load-carrying capacity could be achieved by including 3–5 per cent by weight of an organic phosphate, such as tricresyl phosphate.

It appears that this type of composition has been almost universally adopted in the U.S.A., and a number of very similar oils have been approved against MIL-L-7808 specification. For military purposes, the main object in recent work appears to have been the production of fluids at the lowest possible cost. Sebacate esters have therefore been replaced wholly or partially by azelates, pelargonates, and even adipates, sometimes at the expense of properties such as oxidation and thermal stability. For engines for use in civil aircraft, Pratt & Whitney apply certain additional tests, and therefore have only qualified a proportion of the oils approved to MIL-L-7808, whereas Allison require a 7·5 cS oil to quite a different specification and have only three approved oils.

Turning now to forward-looking specifications for high temperature oils, a target specification, MIL-L-9236, was issued in the U.S.A. in 1954. This called for an oil having quite exceptional viscosity–temperature properties, coupled with, among other tests, a 100-hour bearing rig test with a bearing temperature of 750° F and a bulk oil temperature of 500° F. This specification was superseded in 1956 by MIL-L-9236A, with considerably modified physical test requirements, a bearing rig test at an unspecified temperature, and a " bearing stabilization temperature " test with the oil at 400° F. As this target still was not attained, another specification, MIL-L-25968, was introduced in 1958, this being of considerably reduced severity. This was soon abandoned, however, as a lubricant

was developed with a performance nearer to the MIL-L-9236A level. A new specification, MIL-L-9236B, has accordingly been written round this fluid and has just been published (March 1960). This specification demands a relatively low viscosity oil with good low temperature properties and satisfactory performance in high temperature bearing rigs and in an engine test.

In the U.K. a target specification for high temperature oils, D.Eng. R.D. 2497, was issued in July 1959. The aim in issuing this specification was to provide oils as near as possible in physical characteristics to D.Eng. R.D. 2487 oils, but with much greater thermal and oxidation stability.

A comparison of the physical test requirements of the various high temperature lubricant specifications is given in Table IV.

TABLE IV

High Temperature Lubricant Specifications—Physical Tests

	MIL-L-9236	MIL-L-9236A	MIL-L-9236B	D.Eng. R.D. 2497
Viscosity at 400° F, cS	—	3·0 min	1·0 min	2·0 min
Viscosity at 210° F, cS	10·0 min	Report	—	8·5 max
Viscosity at 100° F, cS	35·0 min	Report	Report	—
Viscosity at −40° F, cS	—	—	—	13,000 max
Viscosity at −65° F, cS	13,000 max	—	—	—
Flash point, ° F	550 min	500 min	425 min	500 min
Pour point, ° F	−75 max	Report	−75 max	—
Spontaneous ignition temp, ° F	700 min	Report	750 min	725 min
Foaming (max values): Sequence 1–2–3 vol, ml	100–25–100	100–25–100	100–25–100	100–25–100
Collapse time, min	5–3–5	5–3–5	—	5–3–5
Evaporation loss (6½ hr at 400° F)	5% max	5% max	15% max	Report

As in the case of D.Eng. R.D. 2487, the new British specification includes tests for shear stability and thermal stability, the former test being conducted using a diesel fuel injector rig at 100° C and the latter using the same procedure as in 2487 but at 325° C instead of 280° C.

The oxidation, corrosion, and thermal stability requirements of these specifications will be considered further later.

LOAD-CARRYING ABILITY

As already pointed out, a certain minimum load-carrying capacity is required of synthetic lubricants in order to provide satisfactory lubrication of the reduction gearing of turbo-prop engines and auxiliary drive gearing.

In the U.K. the IAE Gear Machine has been used almost exclusively for evaluating this property, whilst in the U.S.A. the Ryder Machine has been employed. These machines have been described by Mansion[23] and Ryder[24] respectively.

In the early issues of D.Eng. R.D. 2487, the IAE Gear test was carried out at one speed only, 2000 rev/min, but Issue No. 3 calls for tests at both 2000 and 6000 rev/min with an oil temperature of 110° C, the failure load to be not less than that of a mineral reference oil in each case. This change was made with a view to eliminating certain oils which evidenced an undue falling off of load-carrying ability at high speeds.

Even more severe tests of load-carrying capacity are provided by certain reduction gear power return rig tests devised by Rolls-Royce. One such test involves operating Dart reduction gearing for 150 hours at 15,000 rev/min and 2400 hp with an oil inlet temperature of 115° C. A similar test is conducted on a Tyne reduction gear rig, operated for 150 hours under take-off load conditions. These tests have proved to be exceptionally discriminating, since they provide at the same time tests of the load-carrying properties and of the thermal and shear stabilities of the oils and of any load-carrying additives present. Oils have been known in such tests to fall off rapidly in load-carrying capacity due to thermal degradation of additives present, leading to scuffing of the gears before the end of the 150-hour period. As an additional check, IAE Gear tests are run on the oil after the rig test, to detect deterioration of this kind. Oils submitted for approval against D.Eng. R.D. 2487 are now required to pass tests on the Dart and Tyne reduction gear power return rigs.

In the U.S.A. only Ryder gear tests are carried out. The requirement of MIL-L-7808 specification is not very exacting, but for certain turbo-prop engines oils of higher load-carrying level were found necessary. Another specification, MIL-L-25336, was therefore issued in 1956, the requirements being virtually identical with those of MIL-L-7808, except for the higher failure load on the Ryder machine.

The load-carrying requirements of the various specifications already discussed are summarized in Table V.

TABLE V

Load-carrying Requirements

	IAE Gear Machine, 2000 rev/min and 6000 rev/min	Ryder Gear Machine, 10,000 rev/min and 74° C oil temp
D.Eng. R.D. 2487	Not less than reference oil (oil temp 110° C)	—
D.Eng. R.D. 2497	Not less than reference oil (test oil at 200° C, ref oil at 110° C)	—
MIL-L-7808D	—	68% of ref oil min
MIL-L-25336	—	2800 lb/in min
MIL-L-9236B	—	56% of ref oil min
Pratt & Whitney PWA 521-A	—	1700 lb/in min
Allison EMS-35 G	—	3000 lb/in min

In addition, MIL-L-9236B requires Ryder gear failure loads to be reported using an oil temperature

of 400° F, and there is also a gear fatigue test at this temperature.

The complex esters and polyglycol ethers used in formulating 7·5 cS oils possess a certain indigenous load-carrying capacity. This may be reinforced by including certain very stable chlorine compounds. Diesters by themselves, however, do not have sufficient load-carrying ability, although they are better in this respect than mineral oils for comparable viscosity.[15] In the U.S.A., therefore, tricresyl phosphate has been and is still being used almost universally to provide the necessary level of load-carrying ability for MIL-L-7808.[22]

The attainment of the higher Ryder Gear Machine failure load required by MIL-L-25336 with a 3 cS oil has proved a far more difficult problem. Although a great deal of work has been done, largely in the U.S.A., only one lubricant out of 22 screened had been qualified against this specification in 1958[25] and, as far as the authors are aware, that is still the position. The quantity of oil supplied against this specification is, however, relatively small. The trouble has been that although many additives will provide the necessary increase in load-carrying capacity, they have almost always introduced undesirable side effects, such as increasing the oxidation rate of the oil or attacking metals, such as copper, present in the engine. This is true of the dialkyl phosphites, which have been extensively studied in the U.S.A. by Fenske and Klaus[26] but have had to be abandoned.

Before leaving this subject, one matter deserving of mention is the effect of tricresyl phosphate on the storage life of synthetic oils. Berkey[25] has pointed out that storage instability of MIL-L-7808 oils has been the biggest headache connected with their use. This manifests itself in increasing activity of the oil on storage towards metals, particularly lead. It is known that storage instability can be reduced by using specially purified tricresyl phosphate, but the most effective method is the introduction of a so-called "storage stability inhibitor," which is really an antioxidant effective at low temperatures, and this procedure is now being generally adopted in the U.S.A.

OXIDATION TEST METHODS

A large number of oxidation tests have been applied to the evaluation of synthetic lubricants for gas turbines, but in this section only those which have been embodied in published specifications will be dealt with.

Strictly, the majority of the tests which are to interest us evaluate both oxidation stability and the corrosive tendency of synthetic lubricants. Oxidation stability is generally measured by blowing air (at a definite rate) through a sample of the fluid under test whilst heating at a specified temperature for a specified time. The extent to which deterioration has taken place is then measured in terms of change of viscosity and acidity. In practice, a metal strip is commonly employed to catalyse oxidation during such a test. Certain metals, notably copper, are well known as oxidation catalysts, but, of course, in a gas turbine a variety of metals is present, and it is important to ensure that a lubricant will not give rise to corrosion of engine components. It is with this in mind that many oxidation tests nowadays employ a number of metal specimens submerged in the fluid. The extent of corrosion is then measured by the weight change per unit of area and extent of staining of each metal. From the functional point of view it will be apparent that both significant weight loss (corrosion) and weight gain (deposition) are undesirable, and hence a good lubricant should minimize weight change. Similarly, appreciable staining is generally to be avoided because it is usually argued that this represents only the initial stages of attack of the metal.

A comparison of the conditions of test in six current specifications covering gas turbine lubricants is given in Table VI.

TABLE VI

Comparison of Oxidation Test Conditions

Specification	DERD 2487 (Issue No. 5)	Allison EMS-55G	MIL-L-25968	MIL-L-7808D and MIL-L-25336	Pratt & Whitney PWA-521A
Country of origin	U.K.	U.S.A.	U.S.A.	U.S.A.	U.S.A.
Air-blowing, litres/hr	None	5 ± 0·5	5 ± 0·5	5 ± 0·5	5 ± 0·5
Stirrer speed, rev/min	400 ± 40	—	—	—	—
Metal specimens, area—cm²:					
1. Copper	11·5	13·0	13·0	13·0	13·0
2. Cadmium - plated steel	11·5	—	—	—	—
3. Magnesium alloy	—	13·0	13·0	13·0	13·0
4. Aluminium alloy	—	13·0	13·0	13·0	13·0
5. Steel	—	13·0	13·0	13·0	13·0
6. Silver-plated steel	—	13·0	—	—	13·0
7. Silver	—	—	13·0	13·0	—
8. Titanium	—	—	13·0	—	—
Vol of fluid, ml	400	100 ± 1	100 ± 1	100 ± 1	100 ± 1
Test temp, °C	140 ± 1	175 ± 1	260 ± 1	175 ± 1	126 ± 1
Time, hr	22	72	72	72	168

From the viewpoint of oxidation the least severe test is obviously DERD 2487, which has the lowest temperature, the shortest time, and no air-blowing. The beaker in which this test is conducted is virtually a closed vessel, and hence the volatile products of oxidation are largely retained. Since all other methods shown use air-blowing, this represents a vital point of difference. MIL-L-7808D and Allison specifications embody identical test conditions which are distinctly more severe than DERD 2487. Intermediate in severity is the Pratt & Whitney specification PWA-521A. Most severe of all is MIL-L-25968 (now obsolete in view of MIL-L-9236B), which is included for interest only.

A copper test piece is common to all methods, whereas cadmium plate is specific to DERD 2487 (which is also unique in having only two test metals). It will be noted that American specification tests all

have essentially the same five test pieces, except that MIL-L-25968 has additionally a titanium specimen.

Test conditions taken alone do not, of course, signify much, but need to be considered together with the requirements laid down for the oil after test. Table VII sets out these requirements for the specifications

TABLE VII

Comparison of Specification Requirements

Specification	DERD 2487 (Issue No. 3)	Allison EMS-35G	MIL-L-7808D and MIL-L-25336	MIL-L-25968	Pratt & Whitney PWA-521A
Viscosity change:					
At ° F	100	210	100	100	100
%, max	±5	−5 to +12	−5 to +15	−5 to +300	−5 to +15
Acidity method	IP 139	ASTM D664-52	FS-VVL-791 5105	Electrometric to pH 11	—
mg KOH/g, max	0·5	1·5	2·0	Report	1·0
Corrosion, wt change mg/cm²:					
1. Copper	±0·2	±0·4	±0·4	±1·0	±0·2
2. Cadmium - plated steel	±0·2	—	—	—	—
3. Magnesium alloy	—	±0·2	±0·2	Report	±0·2
4. Aluminium alloy	—	±0·2	±0·2	±1·0	±0·2
5. Steel	—	±0·2	±0·2	±1·0	±0·2
6. Silver-plated steel	—	±0·2	—	—	±0·2
7. Silver	—	—	±0·2	±1·0	—
8. Titanium	—	—	—	±1·0	—
Test temp, ° C	140	175	175	260	126
Time, hr	72	72	72	72	168

considered in Table VI. Again DERD 2487 is evidently the least severe, Pratt & Whitney PWA-521A next, and then MIL-L-7808D. It is noteworthy that the Allison specification requirements are a little more stringent than those of MIL-L-7808D.

Direct comparison of MIL-L-25968 with the others is difficult because of the very high test temperature, but it is certainly the most severe.

All these specifications have been employed to control the oxidation stability of lubricants actually in service, and from this experience it may be said that they have all successfully evaluated the oxidation stability of the lubricants concerned.

However, correlation of the test conditions with those obtaining in service is not very clear. Of course, such a specification only determines whether a lubricant will be serviceable by establishing whether it lies within the fixed boundaries set out in the specification. It does not (and is not generally intended to) indicate, say, the highest temperature at which a given lubricant will remain serviceable.

In contrast to the foregoing, test methods developed by Rolls-Royce set out to determine certain performance limits of the lubricant. These criteria are the "S" temperature, which relates to the limiting bearing oil temperature, and the "B" and "T" temperatures, which relate to the limiting bulk oil temperature.

The "S" temperature is determined by heating a sample of the oil, in a cylindrical stainless steel vessel provided with a close-fitting lid having a single small vent-hole, at a series of temperatures (R.R. Method 1004). The "S" temperature is defined as that temperature at which the benzene insoluble matter in the oil after this test reaches 0·2 per cent w/w after 192 hours. The maximum bearing temperature at which a given oil can be used is considered to be S + 40° C. The test conditions thus involve restricted air supply and are intended to simulate conditions in a hot bearing during "shut-down."

The limiting bulk oil temperature is either the "B" temperature or 25° below the "T" temperature, whichever is the lower. These temperatures are obtained by a method which involves air-blowing a sample in a glass tube at a series of temperatures, and hence is intended to simulate the general bulk oil conditions in an engine (R.R. Method 1001). The "B" and "T" temperatures are those temperatures at which the benzene insolubles reach 0·05 and 0·5 per cent respectively after 192 hours. Both these values are determined by the same method. From a practical viewpoint, it is obviously undesirable to choose a bulk oil temperature at a value near which a rapid rate of rise of insoluble matter occurs for a small increase of temperature. It is in this regard that the "T" temperature is important, because a tenfold increase in insolubles is involved over the "B" temperature. Hence, it is felt that the bulk oil temperature should be chosen at least 25° C lower than the "T" temperature; it may in fact be below the "B" temperature.

In addition to the oxidation test, the Ministry of Aviation have included a thermal stability test in DERD 2487. This test, already described, represents an attempt to separate pure thermal breakdown from breakdown consequent upon oxidation.

Certain American specifications (notably Allison EMS-35) include a panel coking test. In this test an aluminium test panel is heated to 600° F (315·6° C), and oil is splashed thereon for 8 hours under controlled conditions and the weight of coke deposited is recorded. This is obviously a form of oxidation test, but results do not seem very reproducible. In consequence, Wright Air Development Centre (WADC) in the U.S.A. have developed a test apparatus known as the deposition tester. Essentially, this test involves aerating an oil and circulating it past an aluminium coking head held at 590° ± 5° F (310° C) and through a stainless steel 100 mesh filter. The results are quoted as the deposition number (which is the sum of the weight in grams of the filter sludge, and ten times the weight in grams of the coke deposited). Allison's have modified this apparatus by inclusion of a centrifuge in the oil circulating system, which they claim correlates with turbo-prop requirements.

A number of bearing rigs have been used in the evaluation of synthetic lubricants. These are usually under high temperature conditions and are virtually oxidation tests.

One such rig, the Bristol-Siddeley rig, consists

essentially of a 2½-inch roller bearing, lightly loaded and run at 8000 rev/min. Failure normally results from seizure of the bearings due to deposit formation. Since, under the progressive temperature conditions implicit in the test procedure plenty of time is given for build up of " phenothiazine dirtiness " (this term is explained below), the rig is rather in the nature of a sludging test, with the bearing acting like a centrifuge, to collect deposits.

The relatively new British target specification—DERD 2497—involves subjecting the oil to a very much more severe oxidation test. The exact details have not been finalized, but it is believed to involve air-blowing a sample of the oil at 500° F (260° C) (at 12 litres/hour) for 4-, 5-, or 6-hour cycles in the presence of a mild steel catalyst. It is also required that the oil shall perform satisfactorily in a loaded high-speed bearing at an outer race temperature of 325° C (617° F) with an oil inlet temperature of at least 200° C (392° F).

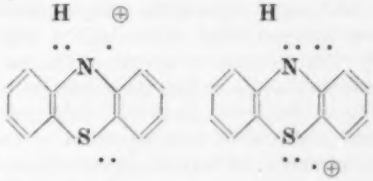
In the U.S.A., MIL-L-9236, which was originally issued as a target specification for high temperature lubricants, has now been issued as MIL-L-9236B. In its latest form no laboratory oxidation test is required, but when a sample of the lubricant is used to lubricate an ERDCO bearing test rig at an oil inlet temperature of 400° F the bearing temperature is required to stabilize itself at 500° F or below. The fluid is also required to operate satisfactorily in a WADC bearing test rig under specified conditions for 50 hours, these conditions being 425° F (218·5° C) bulk oil temperature and 525° F (274° C) bearing temperature.

ANTIOXIDANTS

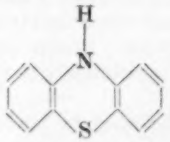
Atkins and co-workers,[7] in their early work in connexion with instrument lubricants, showed that dicarboxylic acid diesters exhibited good response to conventional antioxidants such as secondary aromatic amines and phenols. At higher temperatures these additives were shown by Cohen and co-workers[6,27] to have definite limitations, but phenothiazine and certain of its derivatives gave satisfactory inhibition of oxidation up to 175° C.

A study of phenothiazine and some of its derivatives was published by Murphy, Ravner, and Smith[28] in 1950, and although a vast number of compounds have subsequently been screened as potential antioxidants, it is still used almost universally in ester-based gas turbine lubricants.

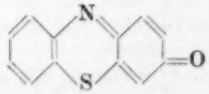
Murphy and co-workers sought to elucidate the mechanism by which phenothiazine acts as an antioxidant and found that it was capable to reacting at 70° C and at 100° C with a very large excess of peroxide oxygen. They postulated a reaction mechanism involving the formation of resonance-stabilized free radicals by the loss of an electron followed by the loss of a proton,



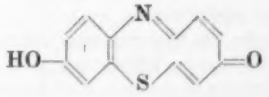
these radicals then reacting with the peroxide radicals formed by oxidation of the ester, with the liberation of molecular oxygen at a relatively low energy level and regeneration, to a considerable extent, of the stabilized free radicals. Since the antioxidant was gradually consumed, the radical regeneration could only be partial, and side reactions were postulated involving both the formation of 10,10¹-diphenothiazine and the oxidation of the phenothiazine ring in the 3- and 7-positions and possibly in the 5-position also. Potential oxidation products of phenothiazine, *e.g.* phenothiazone-3, 7-hydroxy-phenothiazone-3 (thionol), and phenothiazine-5-oxide were all shown to be good antioxidants, as was also 10,10¹-diphenothiazine.



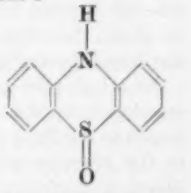
Phenothiazine



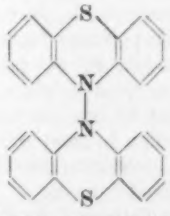
Phenothiazone-3



Thionol



Phenothiazine-5-oxide



10,10¹-Diphenothiazine

All these compounds, however, were less soluble in dioctyl sebacate than phenothiazine itself, and in the oxidation test gave rise either to sludge or heavy lacquer, even at 150° C. Indeed, it seems probable that these compounds undergo further oxidation and dimerization in a manner similar to phenothiazine itself, with the ultimate production of insoluble oxygenated polymeric compounds.

A further study of the oxidation of phenothiazine was made by Cole, Brown, and Schmalz,[29] who showed that the products of thermal and photochemical oxidation were identical and succeeded in establishing definitely the formation of phenothiazone-3- and phenothiazine-5-oxide among the oxidation products. There was evidence to show that the former compound was produced by rearrangement of the latter, with the formation of 3-hydroxyphenothiazine as an unstable intermediate compound. Indeed, it was postulated that this last substance was the real antioxidant, which functioned by reducing free hydroxyl radicals to water and was itself oxidized to a semiquinone or other semi-stable free radical. As an ultimate oxidation product, a black oxygen-containing polymeric substance of molecular weight 1000 to 1200 was isolated from the thermal oxidation products of phenothiazine.

Since 0·5 to 1·0 per cent by weight of phenothiazine is normally used in synthetic gas turbine lubricants, it is not surprising that a gradual formation of "sludge" takes place in service, the rate of formation of the sludge increasing with increasing oil temperature. Engine bearings often act as very efficient centrifuges for this sludge, which accumulates in them and may be heated to temperatures considerably in excess of the bulk oil temperature. Resins and "coke" are thereby formed, leading ultimately to the failure of the bearing.

In practice, of course, oils are screened by laboratory tests or bearing rig tests and the maximum permissible bearing temperature determined for each oil. In effect, therefore, engine design may be, and indeed has been, limited by oil performance.

As a concrete example, an experimental lubricant developed in the author's own laboratory was subjected to the Bristol-Siddeley bearing rig test described in the previous section. This oil was based upon a blend of dioctyl sebacate and a polyglycol ether and contained 1·0 per cent of phenothiazine as antioxidant. Failure of the bearing took place at 250° C, due to clogging by a black powdery deposit which, on analysis, proved to be largely organic in nature, and to contain 11·6 per cent of sulphur. Since phenothiazine (16·1 per cent S) was the only possible source of sulphur, other than in trace amounts, the deposit was obviously an oxidation product or mixture of such products derived from it.

"Phenothiazine dirtiness," as this phenomenon is sometimes called, is also apparent in some laboratory tests. Thus, in the MIL-L-7808 oxidation/corrosion test at 347° F, it appears in the form of dark deposits and lacquer on the test panels, and in the Rolls-Royce confined heat stability test (Method 1004) it shows up in the benzene insolubles.

In the attempt to find better antioxidants than phenothiazine, a vast number of compounds have been screened by Cole and co-workers,[29–33] using an air-blowing oxidation test, generally at 400° F with metals present. In the earlier work[31] an index number of effectiveness was assigned to each oil–additive system investigated under each set of test conditions. This was an empirical number obtained by adding together the weight loss of test cell, per cent viscosity change at 130° F, final neutralization number, insolubles, and total weight loss of metals. It was shown that when the induction period of dioctyl sebacate had not been exceeded the index number remained below 15.

No compounds were brought to light as the result of this work appreciably better than phenothiazine, although N-methyl and N-ethyl phenothiazines appeared to show a slight advantage at 400° F. This was contrary to the findings of Murphy,[28] who found them inferior at 347° F.

However, the N-alkyl phenothiazines, as well as phenothiazine itself, in the concentrations (over 1 per cent) necessary to provide effective inhibition over 72 hours at 400° F, gave rise to substantial amounts of insolubles in the oxidized oil, these being of the order of 2 per cent or more in all tests of 48 hours duration or longer, when metals were present. In fact, in this work the general oxidation inhibiting properties of additives appear to have been studied without particular stress being laid on the problem of insolubles, and many oil-additive systems with low index numbers gave rise to quite high amounts of insolubles.

In the authors' approach to this problem it was considered that if alkyl chains of sufficient length could be attached to the phenothiazine nucleus the oxidation products ought to remain soluble in the ester at least until quite an advanced stage of oxidation had been reached.

It was felt that alkyl chains attached to the nitrogen atom would possibly become detached under oxidizing conditions at high temperatures, and this would result in the same oxidation products being formed as from phenothiazine itself. Alkyl groups attached to the benzene nuclei, however, would be likely to remain attached and to solubilize the oxidation products.

It was surprising that so little attention had been paid by Cole and his collaborators to compounds of this type, but perhaps it was because one such compound, 3,7-dioctyl phenothiazine,[31] did not give very encouraging results. Like many other compounds, however, it had been tested at only one concentration and under one set of conditions, so that the authors were not unduly deterred by this.

As a start, 3,7-dioctyl phenothiazine was synthesized and subjected to various laboratory oxidation tests in dioctyl sebacate and in other esters. Insolubles were indeed almost completely eliminated under the test conditions employed, but it was found that the compound was a less potent antioxidant than phenothiazine itself and that more than the chemically

equivalent amount was required to restrain oxidation to a reasonable degree.

It was soon discovered, however, that greatly improved results could be obtained by using 3,7-dioctyl phenothiazine or other alkylated phenothiazine (Additive Type A) in conjunction with a second additive (Additive Type B) which acted as a synergist. A still further improvement was obtained, especially in the presence of metal catalysts, by the addition of a small amount of a heterocyclic nitrogenous metal deactivator (Additive Type C).

Additive combinations of this type have been tested in a number of different diesters and blended diester-based lubricants with similar results, all MIL-L-7808 oxidation/corrosion tests being characterized by almost completely clean panels with very low weight changes and negligible petroleum ether insolubles. A number of different phenothiazines with oil-solubilizing nuclear substituents have been synthesized and found to behave in a similar manner.

TABLE VIII

MIL-L-7808 Oxidation/Corrosion Tests (72 hours at 347° F)

All additives in di-(2-ethyl hexyl) sebacate

Additives present			Weight change of metal specimens (mg/sq cm)					% Change in viscosity, cS at 100° F	Total acid no. increase	% Insol in petroleum ether (BP 40/60)
			Aluminium alloy	Magnesium alloy	Copper	Steel	Silver			
Phenothiazine (0·5%)			+0·10	+0·09	−0·40	+0·08	+0·17	+ 3·1	1·93	0·50
Type A	Type B	Type C								
1·0	—	—	+0·02	−0·70	− 2·10	+0·06	+0·04	+14·3	16·0	0·50
2·0	—	—	+0·01	+0·03	− 1·20	+0·01	−0·02	+ 6·7	11·1	0·20
3·0	—	—	Nil	Nil	− 1·60	+0·01	+0·06	+ 5·2	•2·9	Nil
—	1·0	—	−0·02	−1·0	−13·0	−0·01	−0·07	+16·5	3·8	0·73
—	2·0	—	−0·01	Nil	− 7·4	Nil	−0·03	+14·0	2·0	0·17
—	3·0	—	−0·01	−10·9	− 8·2	−0·01	−0·03	+23·5	5·6	0·60
1·5	0·5	—	−0·02	− 0·01	− 0·2	Nil	+0·03	+ 4·9	1·57	Nil
1·0	0·5	—	+0·03	+ 0·03	− 1·7	+0·03	Nil	+ 4·7	2·6	Nil
0·5	1·5	—	Nil	Nil	− 3·1	−0·02	−0·05	+ 6·7	1·57	Nil
0·75	0·75	0·1	Nil	+0·01	Nil	+0·01	+0·01	+ 3·0	0·26	0·10
1·0	1·0	0·1	Nil	Nil	− 0·02	Nil	−0·01	+ 4·0	0·92	Nil

In Table VIII are listed the results of MIL-L-7808 oxidation/corrosion tests selected from a very large number of tests carried out on additive compositions of this type.

In this table the blend containing phenothiazine just satisfied MIL-L-7808 specification requirements, but the panels, except the copper, all showed an appreciable gain in weight, due to the deposition of a dark brown lacquer. The petroleum ether insolubles, for which no limit exists in the specification, were quite high at 0·5 per cent for an oil not badly oxidized. The Type A additive, in this instance 3,7-dioctyl phenothiazine, did not approach the effectiveness of phenothiazine itself until 3·0 per cent was present, and even then the acidity and copper loss were outside specification, though the insolubles were reduced to nil. The Type B additive, on the other hand, was a comparatively poor antioxidant, but when the two additives were present together there was a very marked increase in general oxidation resistance, together with complete absence of insolubles. The addition of the deactivator (Type C) effected a manifest further improvement.

The advantage of the new additives at high temperatures was demonstrated by carrying out the very severe MIL-L-25968 oxidation/corrosion test (48 hours at 500° F) on two blends having viscosities of about 5 cS at 210° F and based on a blend of dioctyl sebacate with a high molecular weight polyglycol ether containing a chlorine-bearing load-carrying additive. Blend X contained 1·5 per cent each of additives of types A and B and 0·1 per cent type C, whilst blend Y contained instead 1·0 per cent phenothiazine and 1·0 per cent phenyl-α-naphthylamine with 0·1 per cent type C. Test results on these two blends are summarized in Table IX. Blend Y is included for comparative purposes as an example of a composition closely similar to Blend X, but containing phenothiazine, reinforced with a conventional antioxidant effective over a wide range of temperatures, instead of the combination of additives of types A and B.

It will be seen that Blend X satisfied the requirements, whereas Blend Y did not. Furthermore, there was a marked difference in the insolubles formed from the two oils, and the steel, copper, titanium, and silver specimens from the test on Blend Y were coated with a black deposit which was largely absent from the corresponding specimens from the test on Blend X.

As far as the authors are aware, no diester-based lubricants had previously been successful in passing this test. Indeed, MIL-L-25968 was apparently written round a lubricant based on a trimethylolpropane ester, as it was not believed that the requirements could be met by a conventional diester-based lubricant.

TABLE IX

MIL-L-25968 Oxidation/Corrosion Test

(48 hours at 500° F)

	Blend X	Blend Y	Specification requires
Weight change, mg/sq cm:			
Aluminium	+ 0·20	+ 1·9	±1·0 max
Copper	− 0·22	+ 0·10	±1·0 max
Steel	+ 0·16	+ 1·7	±1·0 max
Silver	+ 0·14	+ 2·0	±1·0 max
Titanium	+ 0·06	+ 0·30	±1·0 max
Per cent viscosity change, cS at 100° F	+37·7	−20·0	−5 to +300
Acidity increase, mg KOH/g	1·51	1·24	—
Per cent insoluble in petroleum ether	2·8	16·1	—

"CLEANER" OILS

A synthetic diester-based lubricant has been developed complying with the physical test requirements of D.Eng. R.D. 2487 and containing additives of types A, B, and C, together with a chlorine-bearing load-carrying additive. This lubricant has been subjected to extensive testing by means of laboratory tests, rig tests, bench engine tests, and in aircraft in flight.

Before this oil was developed, another oil, which was essentially similar except for the antioxidant, had been subjected to the same tests. This earlier oil contained 1 per cent of phenothiazine (purified grade), together with the type C deactivator, but no additives of types A and B.

A direct comparison therefore could be made between these two oils under a variety of test conditions, and some of the relevant results are summarized in Table X, which also includes results obtained on a synthetic reference oil. In this table:

Oil P is the earlier oil containing phenothiazine.
Oil Q is the later oil containing the new additive combination.
Oil R is the reference oil.

It will readily be seen from this table that oil Q was superior to oil P in all respects and was also superior in general to the reference oil. The difference between the S temperatures was much greater than that between the B and T temperatures, however, and the position was summarized by Rolls-Royce, who predicted that the use of oil Q would permit an increase of 15°–20° C in bulk oil temperature and an increase of over 100° C in maximum bearing temperature over the reference oil. This last figure requires some modification, however, since corrosion tests carried out by Rolls-Royce (Method 1002) on oils previously subjected to the 192-hour confined heat stability test (Method 1004) showed that the oil began to become corrosive towards steel after heating at 230°–240° C. The S_c temperature, *i.e.* the S temperature as limited by corrosivity, of oil Q was therefore 230°–240° C, corresponding to a maximum bearing temperature of about 270° C (S_c + 40° C). In the opinion of Rolls-Royce, the difference of 40° C between the S temperature and the maximum bearing temperature applies equally, whether this is limited by deposit formation or by corrosion.

TABLE X

Comparison of Synthetic Lubricants, Oxidation and Rig Tests

Test method	Oil P	Oil Q	Oil R (Average figures)
Rolls-Royce Method 1001 (192 hr air-blowing):			
Temp (*B*° C) at which insolubles reach 0·05%	130	175	145
Temp (*T*° C) at which insolubles reach 0·5%	160	185	185
Rolls-Royce Method 1004 (192 hr confined heat stability):			
Temp (*S*° C) at which insolubles reach 0·2%	150	275	160
Bristol-Siddeley Bearing Rig Test:			
Temp (° C) at which failure occurred (duplicate tests)	250 240	280 270	260

The same three oils were subjected to an accelerated test in a turbo-jet engine employing a total loss lubrication system. These tests were of 24 hours duration with a rear bearing outer race temperature of 260° C. Two tests on oil P failed after 20 and 14 hours respectively, the rear bearing being packed with carbonaceous deposit and the temperature rising uncontrollably. The reference oil R completed the test satisfactorily but the bearing was quite dirty after the test. Oil Q, on the other hand, not only completed the test, but the rear bearing stripped in a comparatively clean oily condition. It was significant that this engine rated the three oils in the same order as the laboratory and rig tests.

Further evidence was obtained from tests on the Allison modified WADC deposition tester, in which oil Q was compared with three other oils already approved to Allison EMS-35 specification. Results are summarized in Table XI.

In the Allison engine, where the oil is subjected to particularly severe oxidizing conditions, the use of oil Q should be especially advantageous.

Oil Q has been subjected to a number of bench engine tests and to flight trials in Rolls-Royce Dart and Avon engines, and the predicted benefits in cleanliness have been realized.

Oils of viscosity 3 cS at 210° F and containing the same additive formulation as oil Q have also been developed and shown by Rolls-Royce and Pratt & Whitney laboratory tests to possess similar advantages over a 3 cS reference oil.

TABLE XI
Allison-Modified WADC Deposition Tests

	Coke deposit, g	Centrifuge deposit	Filter sludge, g
Allison approved oil No. 1	0·17	0·73	0·29
Allison approved oil No. 2	0·09	0·75	0·10
Allison approved oil No. 3	0·11	1·80	0·07
Oil Q	0·05	0·08	0·07

The question of what benefits are likely to accrue in practice from the use of " cleaner " oils in terms of engine overhaul life and oil drain periods must now be considered. This question has been studied by Squires,[34] who has pointed out that when the insolubles level of an oil exceeds 0·2 per cent the engine will be found to be in a rather dirty condition. This condition will not be rectified by draining off the oil, since the sludge will be left in the engine in the form of deposits. Oils containing the conventional antioxidant phenothiazine, after a relatively short induction period, progressively deposit sludge, whereas the new " cleaner " oils are characterized by having a considerably longer induction period during which there is no build-up of sludge. Provided, therefore, the oil is drained before the end of the induction period is reached, engines lubricated with the " cleaner " oils will be maintained in a clean condition and the engine overhaul life, where this is limited by the lubricant, should be prolonged. The maximum benefit from the use of the " cleaner " oils is likely to be observed in those engines with relatively hot bearings whose useful life is limited by deposit build-up.

FUTURE DEVELOPMENTS

No antioxidants, however efficient, can enable a particular base fluid to perform satisfactorily beyond a certain critical temperature.

In the opinion of Squires,[34] an oil such as oil Q could be used in aircraft operating at speeds up to Mach 2·5 provided a total loss system or turbine refrigeration were employed. With both turbine refrigeration and a total loss system, it could probably be used in Mach 3 aircraft.

It is clearly desirable, if possible, to use a normal circulation system without refrigeration, but for Mach 3 aircraft this would involve the use of oils of the D.Eng. R.D. 2497 type. In terms of the Rolls-Royce tests, this necessitates a " B " temperature of at least 240°–250° C and an " S " temperature of 300°–325° C.

As already indicated, it is doubtful whether such temperatures can be achieved even with " hindered " esters, but other types of compounds have been and are being studied, from one or more of which it is possible that lubricants having the desired properties may be developed. Without going into detail, mention may be made of work done by Raley[35] on chlorine-bearing aryl phosphates, by Brown and Holdstock[36] on chlorophenyl silicones, by Rosenberg and co-workers[37] and by Adams and Baum[38] on silanes, and by Ballard and Sommers[39] on fluoresters. The most promising materials to date, however, appear to be certain *m*-polyphenyl ethers described by Mahoney and co-workers.[40]

As an intermediate type of lubricant for aircraft with speeds up to Mach 2·5 with a normal non-refrigerated circulatory lubrication system, it is likely that oils based on " hindered esters " can be used.

Fortunately, the same types of antioxidants that have proved beneficial in the simple diesters can also be used in the " hindered " esters, although the authors have found particular combinations of additives, differing from those in oil Q, to be specially effective in these latter. This is illustrated in Table XII, which summarizes a series of simple tests by Rolls-Royce Method 1001 at 220° C in which air-blowing was continued until solidification of the oil took place.

TABLE XII
Oxidation Tests at 220° C

Oil composition	Test duration, hours	Volatility loss, %
Oil Q	48	72
" Hindered " ester with additives as in oil Q	73	41
" Hindered " ester with special additives of types A and B	180	43

Work in this field is continuing unabated, and it is hoped that before long still more effective combinations of oils and additives will be found.

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DISCUSSION

B. T. Fowler (Esso Research Ltd): Ten years ago, at about the time when the plant production of synthetic aviation turbine oils first commenced in the U.K., there was a number of papers on the subject of gas turbine lubrication. It is, however, at least five years since the topic was reviewed at a meeting such as this. The authors and the IP are therefore to be complimented in presenting us with this opportunity.

I would like to divide the topic into two parts, namely, the review section and the authors' original work. In the review section of the paper the authors have rightly recorded that research in the 1940s proved sebacate-based diester and complex esters stood alone in providing optimum physical characteristics—high VI, low volatility, and high load-carrying capacity.

These oils formed the bases of the MIL-L-7808 and DERD-2487 specifications some eight years ago. Of the 96 airlines operating turbine-powered aircraft to-day, 87 operate exclusively on sebacate diester/complex ester-based lubricants, with another four operating a part of their fleets on these same oils. Five airlines remain in the wilderness.

These figures represent many millions of hours flight experience which cannot lightly be discarded. As the authors mention, in many cases oil drain periods have been extended to coincide with engine overhaul life. A figure of 2000 hours is quoted in the paper. Quite recently one operator of Viscount aircraft extended this period to 3000 hours, and is now beginning further flight trials to extend this period to 4000 hours. So we are still learning about the limits to which we may push the first generation of synthetic oils.

It is, however, clear that certain engines now under development present new challenges to the lubricant technologist. Existing lubricant formulations will not meet the more stringent requirements of the new U.K. and U.S. target specifications.

To-day, with the DERD-2497 and MIL-L-9236B specifications, the accent is on stability—oxidative and thermal—and load-carrying capacity. The authors'

paper presents one approach to the problem of lubricant stability, and in the interest of brevity I shall confine my comments to this aspect of oil quality.

In its simplest form the art of formulating a new lubricant is one of matching base oil components with each other and with additives to strengthen particular features of the base oil blend. Table IX of the printed paper best illustrates the authors' achievements in this field.

Before discussing Table IX there is, however, one point which I would like to mention relating to Mr Elliott's comments in his presentation regarding phenothiazine. Mr Elliott has painted a black picture for phenothiazine as an anti-oxidant for synthetic aviation turbine oil. It is true that the oxidant products of phenothiazine are relatively insoluble and lead to high benzene insoluble figures on used oils. There is, however, one other point regarding phenothiazine as an anti-oxidant which should be mentioned. Many of its oxidation products are themselves anti-oxidants; thus in terms of efficiency phenothiazine has much to commend it.

Returning now to Table IX, blend Y, containing phenothiazine and forming oil insoluble oxidation products, shows a high insolubles content and appreciable viscosity decrease after 48 hours, 500° F oxidation corrosion test. Thus, although oil acidity is efficiently controlled, deposits are formed on the test pieces and in the oil. Also the anti-oxidant does nothing to combat the poor thermal stability of the polyglycol ether base oil component; hence the 20 per cent viscosity loss during the test. In blend X, however, with the authors' approach to anti-oxidants there is a low insoluble content and a 38 per cent increase in used oil viscosity. Here I believe the oil soluble oxidation products provide a thickening effect which more than compensates for the poor thermal stability of the polyglycol ether base oil component. I suggest that if the additives of blend Y were tested in a wholly sebacate-based lubricant, used oil viscosities would show very marked increases and low temperature fluidity of the used oil would be ruined. The results listed in Table VIII are, I believe, obtained under too mild a temperature condition to show whether this is indeed the case, although, with but one exception, all the results tend to suggest that it would be so.

Blend X shows a copper test piece weight loss, which is something I find of interest. While we are all familiar with the mode of action of metal deactivators, it is only quite recently that the behaviour of the metal chelates has come under the microscope. Copper chelates of certain metal deactivator types have very low solubilities which are very much dependent on the hydrocarbon composition of the solvent for which the solubility is determined. I wonder if the authors have any data on metal chelate solubilities in oils of type X, petroleum ether, or benzene. This is a case in point where laboratory assessment of an oil could be giving a false picture, since it is my experience that benzene in particular is a very powerful solvent for copper/MDA complexes, and should these same complexes be rather oil insoluble (in service they would be likely to show up as engine deposits), the benzene insoluble test would give a false impression of lubricant cleanliness. Can the authors tell us whether engine experience on oils of type Q is bearing out the laboratory assessment of the product? I ask this question since I am a little perturbed that so many of our laboratory and rig criteria of oil performance are based almost wholly on a background of phenothiazine inhibited lubricants. It is unfortunate that the developments of laboratory prediction tests remains an art and not a science.

There is one point on which I would like some clarification. On p. 42 the authors point out that the polyglycol ethers are more susceptible to oxidative and thermal breakdown than diesters. On p. 43, however, they mention that blends of diesters and polyglycol ethers may be prepared which are free from problems of shear and thermal instability. My own experience is that ethers are more prone to shear, thermal, and oxidative breakdown than sebacate diesters.

J. S. Elliott: I do not wish to be too hard on phenothiazine, which has done excellent service, and I know that some of its oxidation products are anti-oxidants in their own right. However, when these become insoluble in the oil, they must lose their efficiency to a large extent.

Table IX has been under review. In the first place I should point out that blend Y was not something which was thought up with this paper in mind. It happened to be a blend which we tested in the course of our work on high temperature lubricants, and was the only one that was at all suitable for the kind of thing we wanted to illustrate, so we included it. We abandoned the use of this test procedure when MIL-L-25968 specification became obsolete, because we had plenty of other work on hand. It would have been much better, I agree, if a different composition had been chosen, but we chose that one because we knew the value of phenyl-α-naphthylamine at high temperatures; in fact, we knew that a hindered ester containing phenyl-α-naphthylamine had almost got by the MIL-L-9236B requirements. So we thought that if we mixed that with phenothiazine, we might get an oil with a chance of meeting this specification. That was the reason why this rather peculiar composition was chosen.

The next point is about the viscosity decrease of blend Y. Mr Fowler has made the suggestion that the polyglycol ether component is thermally unstable. I gather, if I understood him rightly, that he thinks that this decrease is offset, in the case of blend X, by oxidation products which are taken into solution to provide this large increase in viscosity I am afraid I do not agree that that does happen.

This takes us to the last remark which Mr Fowler made. We have actually shown that if one takes the thermal stability test which is in DERD-2487 specification, often referred to as the Farnborough test, which involves heating the oil under a nitrogen atmosphere at 280° C, the polyglycol ethers are less thermally stable in general than the diesters. Surprisingly, however, if our new anti-oxidant combination is used, the viscosity decrease that one would normally obtain with a blend of, say, di-octyl sebacate, polyglycol ether, and phenothiazine does not, in fact, take place. I can assure you that no one was more surprised than I when we discovered this, but it would certainly seem that in some way or another these additives not only inhibit oxidation, but thermal breakdown as well. I could produce figures to show that.

On the question of metal deactivators, I cannot say that we have done a great deal, but we know that it is extremely important to select the deactivator correctly.

If one has a deactivator which produces metal complexes which are soluble in the oil, then the result is usually far worse than if it is left out. So that it is necessary to have a deactivator which produces a really insoluble film on the copper specimen.

We have not much experience with different solvents. Normally petroleum ether is used, as in the MIL-L-7808 oxidation test, but the Rolls-Royce tests require the use of benzene, so that we have some experience with the use of both solvents, but we have not really made a study of the effects of different solvents on insolubles.

P. E. B. Vaile (Mobil Oil Co. Ltd): I should like to congratulate the authors on an interesting paper, and it is evident that they and their company have developed a useful additive combination which permits significantly improved performance with diester-based lubricants. I am sure that this will also be a useful reference paper in view of the background information provided on the development of synthetic base fluids and military and civil specifications.

We are still confronted with the use of both 3-cS and 7·5-cS products, and this is not only the result of differing requirements for turbo-jets and turbo-props, but in the U.K. both the military and the engine builders have requested 7·5-cS products for both engine types. Also, we are now at a stage where the severity of both military and civil requirements is increasing, and this may add to the number of products required if increased costs are involved.

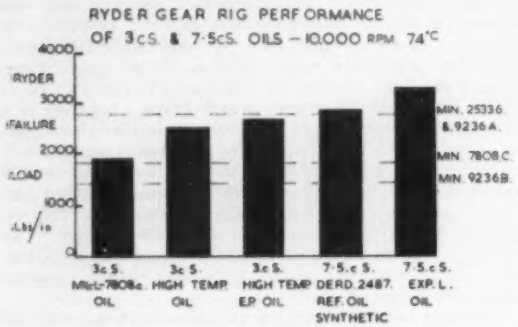


FIG A

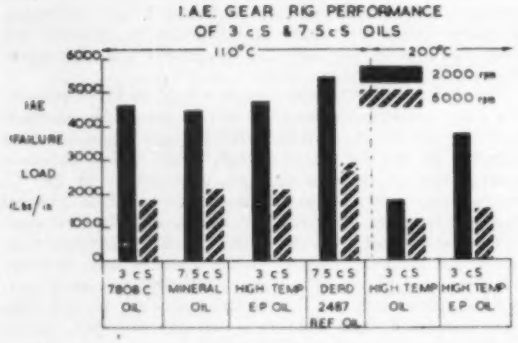


FIG B

Considering first the civil airlines, many run with mixed fleets of both British and American engines, and they would naturally prefer one oil for all engines. Some theatres of operation still have low temperature requirements in the region of −50° to −65° F, and such temperatures can be catered for only by 3-cS oils. Recently, Rolls-Royce have indicated that they are agreeable to operators using approved 3-cS products in their turbo-jet engines if they so desire, and we are therefore left with the question "Can turbo-props operate on 3-cS oils?" before we can decide whether viscosity standardization can be achieved.

In this connexion it may be of interest to record that Allison turbo-prop engines of the U.S. Air Force are operating on 3-cS MIL-L-7808C oils without experiencing any unusual maintenance problems, although it is appreciated that Rolls-Royce turbo-prop maintenance schedules are somewhat more stringent. Following on this, you may be interested to observe from Fig A that it is possible to produce a 3-cS EP product, possessing high temperature characteristics, which gives Ryder gear rig performance superior to that of MIL-L-7808C oils and approaches both the performance of the 7·5-cS DERD-2487 synthetic reference oil and MIL-L-25336 requirements.

Fig B shows IAE gear rig data on 3-cS and 7·5-cS oils, and indicates that at 110° C the 3-cS high temperature EP oil again provides superior performance to a 3-cS MIL-L-7808C oil and approaches the range of results obtained by the 7·5-cS DERD-82487 synthetic reference oil. It is also interesting to note that quite reasonable performance is obtained at 200° C on the 3-cS high temperature EP oil, and that its performance over the 3-cS high temperature synthetic base oil is considerably enhanced when compared with the Ryder gear rig results on these two oils at the lower temperature of 74° C.

The standard Ryder and IAE gear rig tests do not cater for fatigue pitting, which might possibly occur in turbo-prop gearing after continuous running on 3-cS oils. Table A shows that the 3-cS high temperature EP oil

TABLE A

Performance of 32-cS High Temperature EP Oil in Pratt & Whitney Pitting and Scuffing Test

Test conditions: 100 hr at 10,000 rev/min, 3300 lb/in, and 74° C.

Oil	Pitting		Scuffing	
	Requirement	Result	Requirement	Result
High temp 3-cS EP oil	Max of 3 visible pits on non-adjacent teeth	Negligible	55–60% max	42%

meets the requirements ofthe Pratt & Whitney pitting and scuffing test, which usually rejects 3-cS MIL-L-7808C oils.

I also understand that the only 3-cS oil ever approved against MIL-L-25336 has been evaluated in the Rolls-Royce Dart reduction gear power return rig, and the gears were in a satisfactory condition at the end of the test.

In view of the increasing temperature requirements of both turbo-prop and turbo-jet engines, it is interesting to note that the 3-cS experimental high temperature EP oil referred to was designed for at least 400° F (204° C approx) bulk oil operation. Table B indicates its high temperature properties, and although it was not specifically designed to meet the MIL-L-9236B specification, its characteristics are shown against this specification where applicable for guidance purposes.

Such a product could be produced at an economic price, and there would therefore appear to be some scope for developing a 3-cS type oil which could cater for both current and future requirements of turbo-props and turbo-jets in the civil airline field. In saying this I appreciate that with an early mark of one British turbo-prop it would be necessary to modify the propeller control unit and perhaps the main pump capacity before operation on a 3-cS oil.

With regard to military specifications, I feel that in the U.K. any viscosity standardization towards a 3-cS product will be more difficult to achieve, and will certainly not precede any civil airline developments. However, it is interesting to note a trend, in so far as the

TABLE B

Characteristics of High Temperature EP Oil

	3-cS high temp EP oil	MIL-L-9236B requirements
Viscosity, cS:		
At 400° F	1·3	1·0 min
At 210° F	3·96	—
At 100° F	18·26	Report
At −40° F	3,758	—
At −65° F	29,300	—
Pour point ° F	< −65	−75 max
Spontaneous ignition temp, ° F	750	750 min
Panel coker—8 hr at 700° F, mg	150	—
Evaporation loss—6½ hr at 400° F, %	3·5	15 max
Thermal stability—viscosity increase after 24 hr at 536° F, %	0·1	—
WADC deposition test—12 hr at 590° F:		
Deposition No	4·6	—
Neut No increase	1·9	—
Bearing test—Bearing at 500° F, sump at 460° F, air flow 42 l/min:		
Test life, hr	90	—

DERD 2497 specification permits a somewhat lower viscosity product than the DERD 2487 specification.

J. S. Elliott: Mr Vaile has presented us with quite a mass of data, which will repay further study. The only point I will comment on is that we have always understood that the main objection to 3-cS oils has been this question of bearing fatigue, and it is very interesting to note that an oil appears to have been formulated which overcomes this problem. I do not know whether this is a function of the EP additives. Certainly I have always understood that bearing fatigue was purely a function of oil viscosity, but it is possible that additives may affect it, and the figures which Mr Vaile has produced would seem to indicate this. At the moment, as far as I know, there is no inclination on the part of the Ministry of Aviation or Rolls-Royce towards 3-cS oils in the U.K., but it is always possible that they may change. The high temperature target specification DERD-2497 requires an oil of 2·0 cS minimum at 400° F, and I understand that the Ministry of Aviation would not contemplate much relaxation in this figure.

S. R. Pethrick (British Petroleum Co. Ltd): I should like to add my congratulations to the authors for the successful outcome of their work to develop a satisfactory gas turbine lubricant, particularly, as someone said to me one day, as all the simple experiments have already been carried out! I want, therefore, to confine my remarks to some fundamentals in the background of the development of such oils, in particular for the development of oils to the latest Ministry of Aviation high temperature specification.

Whilst I would say that it is true that if an ester is thermally stable at 325° C, it will probably be what the authors call a hindered ester, it is not true that because an ester is a hindered type, it will be stable at 325° C. To illustrate that, we compared two materials (two complex esters) from the same raw materials. One showed a maximum viscosity change of 2 per cent in the Ministry of Aviation high temperature thermal stability test, whilst the other one decreased in viscosity by 18 per cent. There are still a lot of tricks of the trade when using hindered esters.

Another point I would like to make is that I am not quite convinced that when putting an alkyl group or two alkyl groups on to phenothiazine it will automatically increase the solubility of the oxidation products. There is a complication because it is possible that in putting the alkyl groups in the 3 and 7 positions, as the authors have done, one blocks the most vulnerable points of oxidation of phenothiazine.

I also feel that the authors rather summarily dismiss the utility of the *n*-alkyl phenothiazines as anti-oxidants at high temperatures. The mere fact that the alkyl group is easily split off at high temperatures is all the more reason why it should be a more effective anti-oxidant, as it will be forming a resonance stabilized radical. We have found, as have the Americans, that the anti-oxidant known as 5–10–10, *i.e.* 5-ethyl 10–10-diphenyl phenazasilane, is an excellent anti-oxidant at high temperatures. In this case, one has the alkyl group on the nitrogen, and also a multiplicity of phenyl groups to give resonance stabilization.

As with the first speaker, I am not at all happy with the data in Table IX. Maybe we still have something to learn, but I feel that the results are really complicated by thermal instability; their lubricant Y shows thermal instability, and the anti-oxidant combination has not decreased the extent of oxidation markedly.

I am afraid the last point may be rather naughty, but I would like to ask the authors whether, in fact, they have any theoretical basis for the synergistic effect of additives A and B, or was it, as I rather suspect, that additive A was made from additive B and was not pure when first tested.

J. S. Elliott: First of all we have also found that hindered esters have varying stability, and I think the method used, particularly the catalyst used in the preparation, is of vital importance.

It is an interesting point that Mr Pethrick has made about the 3, 7 positions in the phenothiazine ring and he may well be right.

As to the *n*-alkyl phenothiazines, we have no doubt that they are effective anti-oxidants, but the point that we made was that we felt that, if the alkyl group comes off, one will have the same oxidation products that phenothiazine gives, which will be just as insoluble as those derived from phenothiazine itself. Therefore, even though the general oxidation resistance may be good, there would still be an undesirable sludge build-up.

With regard to Table IX, I will not say much more, except that in this type of composition, *i.e.* blends of diesters and polyglycol ethers, I am sure that the drop in viscosity comes after a certain degree of oxidation has been reached. In other words, if one obtains a negative viscosity, it is an indication that the oxidation has proceeded a fair way.

Finally, I would not like to say that there was any theoretical basis for using the mixture of anti-oxidants. On the other hand, it is not true to say that we started off with an impure mixture. We tried a number of things

together hopefully, for I am afraid much of this work is empirical, and we stumbled on this combination.

E. D. Edwards: As far as I know, it would be difficult to synthesize something like 5–10–10 without utilizing an *n*-alkyl derivative. I rather suspect that is the reason why the *n*-ethyl residue appeared at all in 5–10–10.

B. T. Fowler: There is a more general question that I would like to put to the meeting. We have talked a lot about oil cleanliness to-night, and I would like to ask whether, so far as our new specifications are concerned, cleanliness is indeed next to godliness? Should our target for the future be a product with good all-round physical and chemical properties which will provide as clean an engine condition as possible? Does it matter whether one has, say, a relatively dirty oil which produces soft carbon and does not seriously interfere with bearing performance? This, I can imagine, would prove to be a better oil than one which produces a minor amount of hard carbon.

J. S. Elliott: All I can say to that is that certainly a good lubricant is what is needed, but if we can get a clean one as well, without producing hard carbon, why not?

J. L. Heaton (Esso Petroleum Co. Ltd): I cannot help suggesting that Mr Elliott slipped in a crafty one in saying that phenothiazine was dirtier than a combination of A, B, and C. I think he might find that some of the modern versions of phenothiazine and of products containing it are quite as clean as the A, B, and C combinations. I wonder if he would care to deny that?

J. S. Elliott: Most of our work was done with a purified grade of phenothiazine and whilst I quite believe that the purity of the phenothiazine used can influence cleanliness to some extent, I do not see that it can make all that much difference. After all, the principal oxidation products must be the same in any case.

The meeting then closed with a hearty vote of thanks to the authors.

CONTRIBUTED DISCUSSION

R. W. Morton (Esso Research Ltd): I am surprised at the claims made by the authors for phenyl-α-naphthylamine. My original work on synthetic lubricants involved tests on a wide variety of anti-oxidants, including this and several of its analogues. In complex ester/diester blends they were inferior, and I therefore rejected them in favour of phenothiazine. I do not necessarily believe that every compound of this type is inferior to phenothiazine, as obviously I could not test them all, but I found that in general this class of anti-oxidant gave worse and harder carbon deposits than phenothiazine.

J. S. Elliott: I am not aware that we have made any particular claims for phenyl-α-naphthylamine except to mention, as is well known, that it is effective as an anti-oxidant, at least to some extent, over a wide range of temperatures. We agree that it is inferior to phenothiazine in diester-based lubricants.

One point which seems to require further comment is Mr Fowler's criticism of polyglycol ethers on the grounds of shear and thermal instability.

We have not, in fact, found them inferior to diesters in shear stability, although they are somewhat more susceptible to oxidative and thermal breakdown. These latter defects can be corrected by the use of carefully chosen additives, and the paper itself provides ample evidence of the oxidation stability of such oils.

That the additives present can and do also affect thermal stability is demonstrated in Table C, which summarizes test data obtained on oils P and Q in the DERD 2487 thermal stability test at 280° C.

TABLE C

Thermal Stability at 280° C

Change in viscosity at 100° F (%) after	Oil Q	Oil P	Specification requirements
6 hr	−1·9, −1·5	Maximum	Within the limits
12 hr	−0·2, +3·4	Viscosity change	−10% to +20% at all times
18 hr	−0·9, +1·2	−12·0%	
24 hr	−2·6, +3·6 (Repeat tests)		

The shear stability of oil Q was such that there was no decrease in viscosity after 249 cycles in a diesel fuel injector as specified in DERD 2487, Issue No. 4.

LOW-TEMPERATURE FLOW PROPERTIES OF RESIDUAL FUEL OIL: REPORT OF IP FUEL OIL FLOW PANEL

SUMMARY AND CONCLUSIONS

This report reviews the work done by the Fuel Oil Flow Panel, which was set up in December 1949 to devise a laboratory test for predicting the lowest temperature at which a residual fuel oil in normal commercial storage may be pumped or otherwise moved at an economical rate under typical conditions of handling in practice.

It is well known that the viscosity of a fuel oil at storage temperatures can be reliably estimated by extrapolation from known values of the viscosities at higher temperatures, provided that the storage temperature concerned is above that at which any wax present starts to separate. When wax separates, the effect on the flow properties of the oil depends on the age of the oil and the thermal changes that have occurred in storage. The rate at which the oil can be pumped in this condition will depend on the temperature and shearing stress applied, and the test under consideration is required for oils which may reach this condition in storage.

It was supposed by the Panel that a suitable pumpability test would consist essentially of two parts:

(1) a thermal pretreatment of the test sample of oil to simulate the effects of storage conditions in practice;
(2) an estimation of the mobility of the pretreated sample at different temperatures under a shearing stress related appropriately to the mechanical conditions applying in practice.

From field surveys it was decided that a shearing stress of about 300 dynes/cm^2 would be suitable for the test and the analysis of a large number of data obtained on fuel oils in storage in different parts of the world suggested that the thermal pretreatment of the IP upper pour point method provided a suitable means of inducing in an oil a condition similar to that reached during storage in practice. It was subsequently found, however, that in some cases the value of the IP upper pour point depended on the age of the oil, and this suggested that the proposed thermal pretreatment could not be relied upon to induce the aged condition in a freshly blended oil. The Panel therefore started investigations on the change in the IP upper pour point with age, with the object of finding a method of conditioning which would give results independent of the age of the oil. A number of difficulties were, however, encountered in this work, and it was decided to make a report giving a critical review of the problem and the work done by the Panel before proceeding with any further experimental investigations.

In the course of reviewing the work it was realized that although there was substantial evidence of the effect of age on the pour point determined after the thermal pretreatment associated with the IP upper pour point method, it had not been established that this change in pour point was necessarily reflected in an appreciable decrease in the mobility of the oil, when tested under shearing stresses of the magnitudes normally applying in practice.

It is recommended that the particular question of the effect of the age of the oil on its mobility after heat treatment should be investigated by the Panel before deciding whether the problem of devising a satisfactory pumpability test should be further investigated. If work on freshly blended oils and on the same oils after aging should show that the mobility after the thermal pretreatment of the IP upper pour point method does not change very much with age, it would seem that the original plan to use this thermal pretreatment in a pumpability test would be justified. If, on the other hand, a considerable effect of age was observed, the advisability of pursuing the problem would need to be carefully considered.

INTRODUCTION

THE Fuel Oil Flow Panel was set up in December 1949 in response to a general feeling that a study should be made to determine the tests necessary to assess the flow characteristics of fuel oils in relation to practical applications. The terms of reference given to the Panel by the Fuel Oil Sub-Committee were:

"To study the methods of determining the flow properties of fuel oils showing non-Newtonian flow."

It was understood that this statement had been intentionally framed in very general terms so that the Panel should be free to follow any course which their detailed consideration of practical requirements might suggest.

At the inaugural meeting of the Panel it was arranged that members should submit statements of their appreciations of the flow problems arising with fuel oils and that these should be used as a basis for discussions to decide on a programme of work to be followed by the Panel. Four such statements were received. One of these was submitted by the Admiralty representative, one by the research laboratory of an oil company, and two by oil company representatives familiar with the technical aspects of commercial handling. They were considered at a Panel meeting held in June 1950.

The Admiralty statement referred to conditions occurring in ships and in shore storage installations. It was indicated that tests were needed to provide the basis for specifications that would ensure that unheated oil could be transferred at all times at the full capacity of the pumps, with no delay in obtaining suction. It was emphasized that in shore storage oil might lie undisturbed for long periods (years) at low temperatures, so that any effects of age on the properties of the oil would be of great importance.

The statement giving the view of the research laboratory emphasized the sensitivity of the consistency of some types of fuel oils to thermal history and suggested that possible changes in the condition of an oil sample after sampling must be taken into account and eliminated, by some suitable thermal treatment, before making laboratory tests designed to

assess the flow properties of oils in relation to practical performance.

The appreciations of the problems encountered in commercial practice stressed the complexity and variety of conditions under which fuel oils are handled and mentioned the difficulties in attempting to predict the lowest temperature at which satisfactory handling of a given oil could be expected in practice. It was explained that a viscosity at the operating temperature equivalent to about 10,000 sec Redwood I (24 poise) was usually taken as the highest practical limit for normal handling and pumping and that the temperature corresponding with this viscosity was estimated by extrapolation from viscosity data obtained on the fuel oil at temperatures well above its IP upper pour point. When this extrapolated temperature lay above the IP upper pour point it was assumed that the oil could be handled satisfactorily down to the temperature estimated, but when the extrapolated temperature lay below the IP upper pour point of the oil, there was no well-established means of estimating the temperature at which the oil would cease to be fluid enough for satisfactory handling and pumping. In consequence, there was a tendency to specify IP upper pour points which were lower than the expected operating temperature, in spite of the fact that practical experience had shown that many fuel oils could be pumped satisfactorily at temperatures below their IP upper pour points.

It was concluded from the discussions on the appreciations submitted by members that although the demands of the Admiralty were likely to be more exacting than those of commercial practice, the essential problems were of the same nature in both fields, and it was clear that the existing tests for pour point and for viscosity did not provide an adequate means for predicting the ease with which a fuel oil of any particular test characteristics could be moved in practice at temperatures near to or below the IP upper pour point of the oil. It was decided, therefore, that the broad terms of reference given to the Panel should be limited, in the first place, to an objective which could be stated as follows:

> "To find some test to supplement or supplant information yielded by the usual viscosity and pour point determinations in order that the suitability of the fuel oil for any given set of climatic and handling conditions may be assessed with confidence."

It was also decided that the attention of the Panel should be mainly confined to the problems arising in commercial practice and should not include the consideration of the effects of very long periods (years) of storage such as may occur under conditions of use by the Admiralty.

GENERAL APPROACH TO THE PROBLEM

It was agreed by the Panel that a test method to satisfy practical requirements would be one which would allow a prediction to be made of the lowest temperature at which a given fuel oil in normal storage could be satisfactorily transferred under typical conditions of handling. It was recognized that this limiting temperature would, in general, depend on the age of the oil and its thermal history and also on the mechanical conditions in the system available for the handling operations. It appeared that a method of test taking these factors into account might be developed on the following lines:

(1) Thermal pretreatment of the test sample of oil to induce in it the effects of age and thermal history occurring under typical storage conditions.

(2) Shearing of the conditioned oil sample at a suitable temperature for a prescribed period under a shearing stress appropriately related to mechanical conditions of handling in practice. This procedure would allow for any breakdown of structure which might occur in the initial stages of handling in practice.

(3) Measurement of the viscosity of the worked sample at the temperature of working.

(4) Repetition of procedures (2) and (3) at other suitable temperatures in order to assess the lowest temperature at which the fuel oil could be satisfactorily handled in practice. This would amount to the estimation of the temperature at which the viscosity of the worked sample reached the level equivalent to 10,000 sec Redwood I (24 poise).

It was considered that, before attempting to devise a test method on the lines suggested, the Panel would need to obtain more information on the effects of age and thermal history on the flow properties of oils in normal storage and, at the same time, to study the suitability of laboratory thermal pretreatments as a means of inducing similar effects in a test sample of oil. Since the possibility of breakdown and the extent of breakdown of structure in a gelled oil would be expected to depend on the shearing stress used in the process of working in the laboratory under procedure (2), it was considered that an analysis should be made of the mechanical conditions applying during normal handling operations in practice so that an appropriate shearing stress range could be selected for the test method.

The general programme of work was therefore planned as follows:

(*a*) Examine a variety of fuel oils in normal commercial storage in various parts of the world in order to assess the extent to which their rheological properties had been influenced by age and thermal changes in storage.

(*b*) Study the suitability of laboratory thermal pretreatments as a means of inducing in a test sample the typical effects of practical storage.

(*c*) Survey the mechanical conditions under which fuel oils are handled and pumped in practice.

It was expected that it would take some considerable time to make the arrangements necessary to obtain information on the condition of oils in storage in various parts of the world, and it was therefore agreed to proceed concurrently with the study of laboratory thermal pretreatments and the survey of mechanical conditions in practical handling. It was hoped that the integration of the data obtained under these three headings would provide a basis for the selection of suitable conditions to be applied in a test method on the lines suggested.

EXAMINATION OF FUEL OILS IN COMMERCIAL STORAGE

When a fuel oil is allowed to cool, a temperature is reached at which a solid phase begins to separate. This solid phase, which usually consists of wax associated with asphaltenes and/or other components of the oil, will be referred to as the " waxy phase."

The fluidity of a fuel oil at, or below, the temperature at which the waxy phase first separates will be determined partly by the fluidity of the continuous oily medium and partly by structural effects due to the presence of the waxy phase. It may be assumed that, at any given temperature, the composition and, therefore, the fluidity of the continuous phase will be independent of any thermal changes to which the oil has been subjected, but it is well known that, in many cases, the temperature at which the structural effect of the waxy phase first becomes appreciable is very dependent on the thermal history of the oil. It would be expected, therefore, that any effects of storage conditions on the lowest temperature at which an oil could be satisfactorily handled in practice will be determined solely by the effect of these conditions on the temperature at which the degree of structure imparted by the waxy phase first becomes sufficient to cause a significant decrease in the fluidity of the material.

The IP pour point methods determine the effect of two different thermal pretreatments on the lowest temperature (a multiple of 5° F) at which the oil will pour (*i.e.* the pour point) when it is cooled, without disturbance, under prescribed conditions and tested for flow in a standard way: with most oils this temperature is largely determined by the development of a critical degree of structure due to the waxy phase. With a given oil, the thermal pretreatment used in the test for the upper pour point induces a condition which tends to give the highest possible temperature (highest pour point) at which this critical degree of structure is reached, while the pretreatment used in the test for the lower pour point induces a condition which tends to give the lowest possible temperature (lowest pour point). The difference between the temperatures of the IP upper and lower pour points, with any particular oil, therefore gives a measure of the maximum extent to which thermal history is likely to affect the temperature at which the waxy phase will give a critical degree of structure.

It was thought by the Panel that the thermal changes occurring under any particular storage conditions in practice would probably be equivalent, in their effect on the temperature to give a critical degree of structure, to some short period laboratory thermal pretreatment. It was suggested that if a sample of oil taken from storage were cooled, without any thermal pretreatment, under the standard conditions adopted in the pour point method, the relationship between the pour point determined in this way (referred to as the " as received " pour point) and the IP upper and lower pour points determined on a sample of the same oil at the same time would give an indication of the extent to which the actual thermal history of the oil in storage had affected its subsequent behaviour on cooling in comparison with the effects on the same oil of the thermal pretreatments of the IP pour point methods.

A convenient way of comparing the effect of the actual storage conditions with the effects of the IP thermal pretreatments consists in calculating an index number, which will be termed the " Index of Storage Effect," as follows:

$$\text{Index of Storage Effect} = \frac{(A-L)}{(U-L)} \times 100$$

where A = " as received " pour point;
L = lower pour point;
U = upper pour point.

It is emphasized that the index of storage effect is not essentially a characteristic of the oil. Its value will, in general, depend on the duration of storage and also on the thermal changes during storage.

It was hoped that the information obtained by measuring the index of storage effect on oils in storage in various parts of the world would indicate the typical effects of storage conditions in practice and would provide a reliable basis for the selection of a suitable laboratory thermal pretreatment to simulate these effects in a test sample.

Following these suggestions, IP upper, IP lower, and " as received " pour points were determined on samples of a large number of fuel oils taken from commercial storage, mainly in the distributing depots of oil companies, in as many different localities as it was possible to arrange. Operators were advised to take the samples for the " as received " pour points as gently as possible, in order to lessen the disturbance of any structure present, and it was stipulated that

the " as received " pour points should be determined with the least possible delay after sampling.

No precise information was available in any case on the age of the oil at the time of testing and, in many cases, an estimate of this age could not have had any very definite meaning because of oil movements into and out of the tank. With few exceptions, the average age of the material tested was not likely to have been more than about one month, and some oils were probably not more than a few days old. It may be assumed, however, that the survey adequately covered the range of conditions that normally occurs in distributors' storage.

Samples representing 45 different commercial fuel oils were taken at 15 installations representative of the storage conditions in eight countries (British Isles,

TABLE I

Data on Fuel Oils in Commercial Storage, Grouped According to Location

Ref. No.		Location	Properties of fuel						Storage tank temp, °F	*I*
Fuel	Installation		Sp gr, 60° F/60° F	Visc, sec Red I at 100° F	Pour point, ° F					
					U	*L*	*A*	*B*		
1	1	Australia	—	45	75	75	75	70	88	*
2	1	Australia	0·892	49	70	60	50	80	78	†
3	1	Australia	0·895	50	75	20	60	50	83	73
4	1	Australia	0·892	50	75	45	70	75	98	83
5	2	Australia	0·927	368	60	15	40	25	75	55
6	2	Australia	0·958	400	70	15	25	25	76	18
7	2	Australia	0·972	500	35	10	25	10	97	60
8	3	N. America	0·996	3,600	35	30	35	40	136	100
9	4	N. America	0·986	448	−10	−10	−10	−10	—	*
10	5	Holland	0·937	325	21	−6	10	16	86	59
11	5	Holland	0·951	783	43	16	16	21	84	0
12	6	NWI	0·939	923	10	0	10	0	122	100
13	6	NWI	0·941	921	10	0	10	0	131	100
14	7	Indonesia	0·939	207	45	45	40	60	113	*†
15	8	Egypt	—	1,350	45	30	45	50	—	100
16	8	Egypt	—	3,040	55	35	40	55	—	25
17	8	Egypt	—	400	65	50	55	65	86	33
18	9	Egypt	0·929	420	45	40	25	55	85	†
19	9	Egypt	0·955	1,446	30	25	30	50	102	100
20	10	S. Africa	—	460	65	55	50	65	77	†
21	10	S. Africa	—	580	40	0	10	35	80	25
22	10	S. Africa	—	420	70	55	55	65	77	0
23	10	S. Africa	—	550	45	5	5	40	78	0
24	10	S. Africa	—	250	65	20	55	55	70	78
25	10	S. Africa	—	280	65	35	60	65	70	83
26	11	U.K.	0·925	183	30	<0	15	—	58	50
27	11	U.K.	0·926	360	70	55	65	—	80	67
28	11	U.K.	0·937	555	55	35	45	—	98	50
29	11	U.K.	0·928	357	70	55	65	—	82	67
30	12	U.K.	0·926	360	65	50	60	—	88	67
31	12	U.K.	0·945	850	40	0	35	—	74	88
32	13	U.K.	0·929	360	70	55	65	—	104	67
33	13	U.K.	0·952	876	60	15	50	—	97	78
34	13	U.K.	0·921	190	30	30	30	—	102	*
35	14	U.K.	0·929	396	60	50	50	—	93	0
36	14	U.K.	0·927	363	60	50	55	—	86	50
37	14	U.K.	0·928	350	55	35	45	—	82	50
38	14	U.K.	0·928	390	55	50	50	—	93	0
39	14	U.K.	0·927	359	60	50	50	—	88	0
40	14	U.K.	0·924	181	20	0	0	—	43	0
41	14	U.K.	0·919	192	25	−20	20	—	42	89
42	15	U.K.	0·924	170	10	5	0	—	43	†
43	15	U.K.	0·918	190	30	−20	20	—	50	80
44	15	U.K.	0·917	163	20	5	10	—	52	33
45	15	U.K.	0·925	173	10	5	5	—	45	0

U = IP upper pour point
L = IP lower pour point
A = " As received " pour point
B = Special pour point " B " (see p. 62)
I = Index of storage effect
* = Upper and lower pour points have identical values
† = " As received " pour point below IP lower pour point

Note: Where the pour point was originally recorded in ° C, these temperatures have been converted to ° F.

TABLE II

Data on Fuel Oils in Commercial Storage, Grouped According to Index of Storage Effect

Ref. No.		Location	Properties of fuel						Storage tank temp, °F	*I*
Fuel	Installation		Sp gr, 60° F/60° F	Visc, sec Red I at 100° F	Pour point, ° F					
					U	*L*	*A*	*B*		
8	3	N. America	0·996	3,600	35	30	35	40	136	100
19	9	Egypt	0·955	1,445	30	25	30	50	102	100
15	8	Egypt	—	1,350	45	30	45	50	—	100
12	6	NWI	0·939	923	10	0	10	0	122	100
13	6	NWI	0·941	921	10	0	10	0	131	100
41	14	U.K.	0·919	192	25	−20	20	—	42	89
31	12	U.K.	0·945	850	40	0	35	—	74	88
25	10	S. Africa	—	280	65	35	60	65	70	83
4	1	Australia	0·892	50	75	45	70	75	98	83
43	15	U.K.	0·918	190	30	−20	20	—	50	80
33	13	U.K.	0·952	876	60	15	50	—	97	78
24	10	S. Africa	—	250	65	20	55	55	70	78
3	1	Australia	0·895	50	75	20	60	50	83	73
27	11	U.K.	0·926	360	70	55	65	—	80	67
32	13	U.K.	0·929	360	70	55	65	—	104	67
30	12	U.K.	0·926	360	65	50	60	—	88	67
29	11	U.K.	0·928	357	70	55	65	—	82	67
7	2	Australia	0·972	500	35	10	25	10	97	60
10	5	Holland	0·937	325	21	−6	10	16	86	59
5	2	Australia	0·927	368	60	15	40	25	75	55
28	11	U.K.	0·937	555	55	35	45	—	98	50
36	14	U.K.	0·927	363	60	50	55	—	86	50
37	14	U.K.	0·928	350	55	35	45	—	82	50
26	11	U.K.	0·925	183	30	<0	15	—	58	50
17	8	Egypt	—	400	65	50	55	65	86	33
44	15	U.K.	0·917	163	20	5	10	—	52	33
16	8	Egypt	—	3,040	55	35	40	55	—	25
21	10	S. Africa	—	580	40	0	10	35	80	25
6	2	Australia	0·958	400	70	15	25	25	76	18
11	5	Holland	0·951	783	43	16	16	21	84	0
23	10	S. Africa	—	550	45	5	5	40	78	0
22	10	S. Africa	—	420	70	55	55	65	77	0
35	14	U.K.	0·929	396	60	50	50	—	93	0
38	14	U.K.	0·928	390	55	50	50	—	93	0
39	14	U.K.	0·927	359	60	50	50	—	88	0
40	14	U.K.	0·924	181	20	0	0	—	43	0
45	15	U.K.	0·925	173	10	5	5	—	45	0
9	4	N. America	0·986	448	−10	−10	−10	−10	—	*
14	7	Indonesia	0·939	207	45	45	40	60	113	*†
34	13	U.K.	0·921	190	30	30	30	—	102	*
1	1	Australia	—	45	75	75	75	70	88	*
20	10	S. Africa	—	460	65	55	50	65	77	†
18	9	Egypt	0·929	420	45	40	25	55	85	†
42	15	U.K.	0·924	170	10	5	0	—	43	†
2	1	Australia	0·892	49	70	60	50	80	78	†

U = IP upper pour point
L = IP lower pour point
A = " As received " pour point
B = Special pour point " B " (see p. 62)
I = Index of storage effect
* = Upper and lower pour points have identical values
† = " As received " pour point below IP lower pour point

Note: Where the pour point was originally recorded in ° C, these temperatures have been converted to ° F.

Australia, America, Holland, Netherlands West Indies, Indonesia, Egypt, South Africa). The data obtained on these samples are grouped according to location in Table I and according to index of storage effect in Table II. These data are discussed and summarized below.

The storage tank temperatures recorded in Table I cover a wide range from 42° to 136° F and are in all cases at least 5° F above the IP upper pour point of the oil. On the average, the tank temperature is about 35° F above the IP upper pour point of the oil.

Fig 1 shows a relationship between the viscosity of an oil in seconds Redwood I at 100° F and the temperature at which the viscosity of this oil would be expected to reach the limit for satisfactory pumpability (10,000 sec Redwood I), assuming that the

flow was not influenced by the separation of a waxy phase. This relationship has been obtained by considering typical values for the temperature susceptibilities of oils in the various viscosity grades and it appears that the storage temperatures given

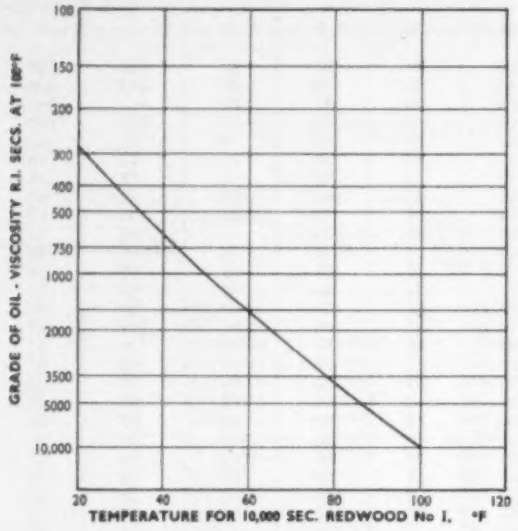


FIG 1

RELATION BETWEEN VISCOSITY GRADE AND ESTIMATED TEMPERATURE FOR VISCOSITY OF 10,000 SEC REDWOOD I

in Table I all lie well above the value estimated for a viscosity of 10,000 sec Redwood I.

The fuel oils listed in Table I can be separated into three categories, depending upon whether the values of their IP upper pour point and " as received " pour point are above or below the estimated lowest temperature for satisfactory pumping given by Fig 1, namely:

(*a*) IP upper pour point and " as received " pour point both below the estimated lowest temperature for satisfactory pumping. In this case the oil belongs to the class in which the pumpability is—" not limited by pour point."

(*b*) " As received " pour point is below but IP upper pour point is above the estimated lowest temperature for satisfactory pumping. In this case the pumpability is—" potentially limited by pour point."

(*c*) " As received " pour point and IP upper pour point are both above the estimated lowest temperature for satisfactory pumping. In this case the pumpability is—" limited by pour point."

In Table III the oils listed in Table I are divided into five viscosity grades and analysed into the three categories just discussed. It will be seen that 35 of the 45 fuel oils considered belong to the categories in which the pumpability is directly limited or potentially limited by pour point, *i.e.* the types of oils for which

TABLE III

Pour Point Categories of Fuel Oils listed in Table I

Category	Number of oils in each viscosity grade (sec Redwood I at 100° F)					Total all grades
	45–50 sec	150–300 sec	300–399 sec	400–600 sec	780–3600 sec	
(*a*) Not limited by pour point	Nil	Nil	1	1	8	10 (22%)
(*b*) Potentially limited by pour point	Nil	3	Nil	5	Nil	8 (18%)
(*c*) Limited by pour point	4	8	10	4	1	27 (60%)

the pumpability test under discussion is required. Of the ten oils in the category in which the pumpability is not limited by pour point, eight were in the most viscous class.

The summary given in Table IV shows the distribution of the pour points among the oils examined. Table V shows that 28 of the total of 45 oils tested gave a difference of 15° F or more between the upper and lower pour points and were therefore of the types most likely to be affected by thermal history in storage. It will also be noted from Table V that

TABLE IV

IP Upper Pour Points of Oils Tested

Upper pour point lying between	Number of oils
55° and 75° F inclusive	23
25° and 50° F inclusive	14
Below 25° F	8
Total	45

TABLE V

Difference between IP Upper and Lower Pour Points

Difference between IP upper and lower pour points	Number of oils	Number of oils " pour point limited "
0°–10° F	17	9
15°–20° F	12	9
25°–30° F	5	3
35°–40° F	4	Nil
45°–50° F	5	5
55°–60° F	2	1
Total	45	27

there is no significant correlation between the difference between the upper and lower points and the distribution of the number of oils which were considered to be " pour point limited." With the 28 oils giving 15° F or more between the upper and lower pour points, as shown in Table VI, the value of the

index of storage effect varied from 0 to 100 with a fairly uniform distribution over the total number of oils.

TABLE VI

Values of the Index of Storage Effect in Stored Oils showing Pronounced Sensitivity to Thermal History (i.e. difference of 15° F or more between upper and lower pour points)

Range of index	Number of oils	Number of oils " pour point limited "
0–20	5	5
21–40	4	3
41–60	6	5
61–80	8	8
81–100	5	3
Total	28	24

Table VII analyses the data of Table I for the 28 oils given in Table VI and shows that no significant correlation could be found between the value of the index of storage effect and any of the data given in Table I. It is possible, however, that a more detailed knowledge of the thermal histories of the oils would have provided an explanation of the differences.

TABLE VII

Comparison of Index of Storage Effect with Other Data for Oils Showing Pronounced Sensitivity to Thermal History

Index range	Average value of data for oils within index range						
	U	*L*	*A*	*T*	*T–U*	*T–L*	*T–A*
0–20	50	18	20	71	21	53	51
21–40	45	23	29	73	28	50	44
41–60	43	18	30	83	40	65	53
61–80	63	31	54	82	19	51	28
81–100	52	18	46	71	19	63	25

U = IP upper pour point, ° F;
L = IP lower pour point, ° F;
A = IP " as received " pour point, ° F;
T = storage tank temperature, ° F.

It may be concluded from Table VI that with oils showing a pronounced sensitivity to thermal history, the effect of normal storage conditions in raising the temperature at which the structure due to the waxy phase first becomes appreciable is, on the average, less than that due to the thermal pretreatment of the oil sample by the IP upper pour point method. However, since the oil had an index number approaching 100 in nearly 20 per cent of the cases being considered, it would appear that a thermal pretreatment equivalent to that of the IP upper pour point method would be necessary to simulate the effect of storage conditions in an appreciable proportion of cases.

For the 17 oils (Table V) which, according to the difference between their IP upper and lower pour points, appeared to have a low sensitivity to thermal history, the value of the index in four cases was 100, while four showed an index of 0 and one an index of 50. In four cases these pour points had the same value, while in five cases the oils gave anomalous results in that the " as received " pour point was below the IP lower pour point. If this anomalous behaviour is ignored, it would appear that with these less sensitive oils also a thermal pretreatment equivalent to the IP upper pour point method would provide a suitable compromise as a means of simulating the effects of practical storage conditions.

LABORATORY INVESTIGATIONS ON THE INFLUENCE OF THERMAL PRETREATMENT ON POUR POINT

In the IP upper pour point method the oil is heated to a temperature of 115° F before being cooled in the standard way to determine the temperature of the pour point.

It was fairly generally known that the method adopted for the IP upper pour point does not necessarily result in the highest pour point which any particular fuel oil can attain as the result of laboratory thermal treatments, and many examples of this were reported by Panel members. The curves of Fig 2 illustrate a type of behaviour which may be frequently observed with fuel oils containing both wax and asphaltenes when subjected to different heat treatment temperatures. The experimental procedure adopted in obtaining these curves consisted in heating each fuel in a 16-oz cylindrical bottle for 15 minutes with stirring at a temperature of 220° F. The bottle was then placed immediately in a bath controlled thermostatically at 77° F and held at this temperature for 90 hours. Samples of this oil were then reheated to the required pretreatment temperature, allowed to cool to 90° F, and the pour point then determined by cooling according to the procedure of IP 15/42.

The curves in Fig 2 illustrate the general tendency for the pour point to increase to a maximum at a heat treatment temperature which is a characteristic of the particular fuel oil and is different with different types of oils. This behaviour indicates that it is unlikely that any thermal pretreatment using the same temperature for all oils would approximate at all closely to the effects of normal storage conditions on different types of oils.

At the time this question was considered, the results of the examination of the condition of oils in storage in various parts of the world were not yet available, and it was considered that some form of thermal pretreatment was required which did not bring the oil into the most favourable condition it could possibly reach (*i.e.* the condition represented by the IP lower pour point) nor into the worst possible

condition (*i.e.* the condition represented by the maximum pour point obtained at the optimum heat treatment temperature in Fig 2), but into some intermediate state which, it was thought, might be a satisfactory approximation to the condition normally reached by the oil in commercial storage.

It was then suggested by a member of the Panel that, from his experience with oils from a certain crude, the type of thermal pretreatment required might be given by the following method:

> Heat the sample to a temperature of 220° F and cool to 40° F over a period of not less than two nor more than four hours.
>
> Reheat the cooled sample to a temperature of 115° F and then proceed according to the IP upper pour point method.

Accordingly, pour point determinations by this method, which is referred to as special pour point "B," were included in the schedule of tests requested in the programme of the examination of oils in commercial storage. The results obtained are included in Table I.

It will be seen from Table I that the special pour point "B" is equal to or above the IP upper pour point for 16 of the 25 oils examined in this way. In most cases, therefore, the thermal pretreatment used in special pour point "B" is more severe than that of the IP upper pour point method, and for this reason was considered to be unsuitable for the purpose required by the Panel.

STORAGE AND HANDLING CONDITIONS IN PRACTICE

In order to have a reasonable basis for the selection of a shearing stress or range of shearing stresses to be used in the rheological measurements on the thermally conditioned sample in a test on the lines under consideration by the Panel, a survey was made of the storage and handling conditions which prevail in practice.

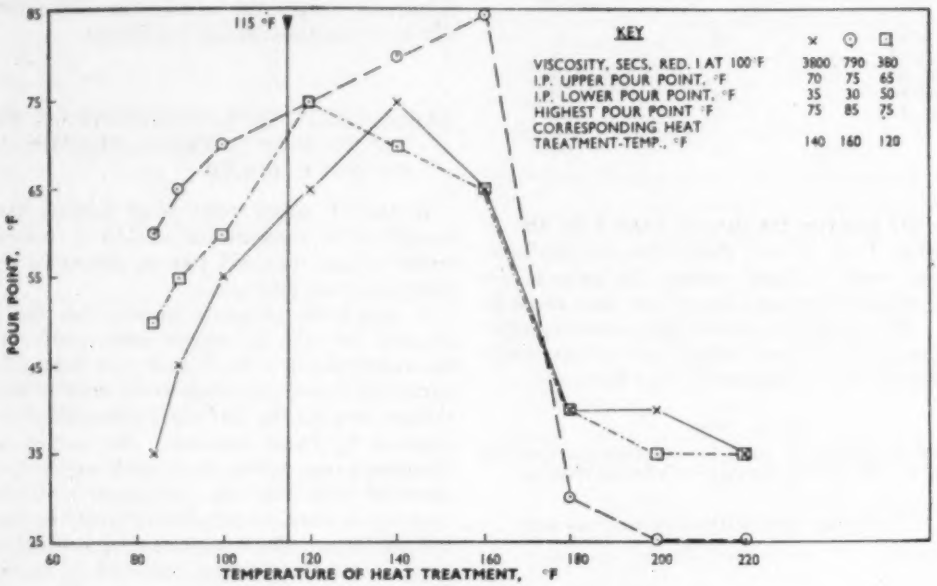


FIG 2

THE INFLUENCE OF THERMAL TREATMENT ON POUR POINT

Data were obtained relating to installations such as tanker, bunker and discharge services, inter-installation transfer lines, drum filling lines, and rail car discharge lines. From the figures supplied for the pressures or suctions applied to the oils, the diameters of pipes, and the normal rates of discharge obtained, values were calculated for the shearing stress at the wall of the pipe, the apparent rate of shear at the wall of the pipe, and the corresponding apparent viscosity. The basic data and the figures derived by calculation are given in Tables VIII and IX.

It will be seen from Table IX that, in order to achieve the rates of discharge quoted in Table VIII, the viscosity of the oil must, in many cases, be appreciably less than the figure of about 10,000 sec Redwood I (equivalent to about 24 poises) which has

TABLE VIII

Typical Conditions of Pumping of Fuel Oil in Practice

Service	Suction side			Delivery side		Pressure, psi	Rate, tons/hr
	Pipe dia, in	Max distance, ft	Max static lift, ft	Pipe dia, in	Max distance, ft		
Tanker discharge	12	300	5	10–12	Average about 5,000	80	200–750
	10–12	200	5	Up to 10	5,000	80	200–400
	8–10	100	5	Up to 8	2,000	80	100–200
Bunkering	12	3,000	Usually flooded suction	10–12	5,000	50–100	200–500
	10	1,500	Usually flooded suction	8–10	3,000	50–100	100–300
Inter-installation transfer	12	500	Usually flooded suction	10	1,000	50	100
	10	300	Usually flooded suction	8–10	500	50	100
	8	200	Usually flooded suction	8	200	30–50	50
Drum filling	6-inch branch from 8–10-inch line	500	Usually flooded suction	4–6-inch branch from 6–8-inch line	200	30	50
	4-inch branch from 6–8-inch line	100	Usually flooded suction	4-inch branch from 6-inch line	200	20	20
Railcar discharge	4	70	Assumed flooded suction	—	—	60	40
Automatic pre-heating burner	1	30	Flooded suction (3 psi)	—	—	—	
Transfer from storage to service tank	—	—	—	6	450	100	20

TABLE IX

Shear Stresses, Apparent Rates of Shear, and Viscosities Derived from Table VIII

Service	Minimum shear stress, dynes/cm²		Apparent rate of shear, sec⁻¹		Viscosity, poises	
	Suction	Delivery	Suction	Delivery	Suction	Delivery
Tanker discharge	960	230	21	37	12	6
	320	230	37	37	9	6
	515	460	36	36	14	13
Bunkering	40	145	21	37	2	4
	65	190	18	35	4	6
Inter-installation transfer	230	720	11	18	21	40
	305	1150	18	18	17	64
	380	1750	18	18	21	97
Drum filling	110	865	42	42	3	21
	380	575	57	57	7	10
Railcar discharge	540	—	115	—	5	—
Automatic pre-heating burner	145	—	—	—	12	—
Transfer from storage to service tank	—	800	—	17	—	5

Shear stress (at wall of pipe.) . . . . . $\frac{Pr}{2L}$ dynes/cm²

Apparent rate of shear (at wall of pipe) . . . . $\frac{4Q}{\pi r^3}$ sec⁻¹

Where P = pressure in dynes/cm²;
r = radius of pipe in cm;
L = length of pipe in cm;
Q = rate of flow in cc/sec.

The pump suction available has been taken as equivalent to 15 ft of water

been suggested as the upper limit for satisfactory pumping. However, it appears that a viscosity as high as 24 poises would not generally cause serious handling difficulties.

While it was appreciated that it might be desirable, in the final testing procedure, to use more than one level of shearing stress, the data presented in Table IX gave an average shearing stress on the suction side of the pump of about 300 dynes/cm² so that this was considered to be an appropriate value to use in the development of the proposed test.

EVIDENCE OF CHANGE IN IP UPPER POUR POINT WITH AGE

From the examination of fuel oils in commercial storage it appeared that although the fuel oil may approach the condition induced by the thermal pre-treatment of the IP upper pour point method it is not likely to reach any worse condition in normal storage. In fact, while the condition of a fuel oil, as judged by its "as received" pour point, may lie anywhere between those corresponding with the IP upper and lower pour points, or even below that corresponding with the lower pour point, it generally

assumes a condition significantly better than that corresponding with the IP upper pour point.

Ample evidence was obtained by the Panel that it was unlikely that a single form of thermal pretreatment could be found which would induce in all fuel oils the same condition as they would have in normal storage.

It therefore appeared to the Panel that, as a compromise, no more suitable thermal pretreatment was likely to be found than that already prescribed in the IP upper pour point method. This induces in a fuel oil a condition which is sometimes reached in practice, although the condition in practice will normally be somewhat more favourable. The fact that the IP upper pour point pretreatment might be somewhat too severe was regarded as providing an acceptable margin of safety in the proposed test method.

At this stage, however, evidence became available to the Panel that the IP upper pour point of some oils could change significantly during the first few days or weeks of their lives. Examples of this evidence are given in Table X, which summarizes data obtained on a total of 71 shipments of the same grade fuel oil from refinery to receiving area.

TABLE X

Change in IP Upper Pour Point during Shipment

(a) IP Upper pour points at time of despatch

	Number of oils
Upper pour points lying between:	
30° and 35° F, inclusive	2
40° and 45° F, inclusive	16
50° and 55° F, inclusive	32
60° and 65° F, inclusive	21
	71

(b) Difference between IP upper pour points determined immediately before despatch and immediately after delivery

Change in pour point:	
+10° F, or more	35
+5° to −5° F	28
−10° F or more	8
	71

Pour point observations were made on shore tank samples immediately before despatch and immediately after delivery, the interval between the two determinations being about three weeks; the 71 shipments were made over a period of three years. It will be observed that these data provide evidence of both increases and decreases in pour point with age.

Table XI records the observation on a sample of freshly prepared fuel oil stored in a refinery laboratory at normal laboratory temperature. The data show that the fuel behaved erratically for about a fortnight following preparation and then assumed an IP upper pour point significantly greater than that exhibited on preparation.

Table XII records similar observations on a different fuel oil stored at another refinery. For this fuel the "as received" pour point increased slowly from −3° to +15° C, while the IP upper pour point increased only from 18° to 21° C during the same period (some 45 days). A similarly stored fuel of different composition was reported by the same refinery as showing an increase in "as received" pour point of 24° C (−3° to +21° C) and an increase in IP upper pour point of 6° C (15°–21° C) over a period of some 40 days.

TABLE XI

IP Upper Pour Point Behaviour of a Freshly Prepared Fuel Oil Stored in Bulk at a Refinery Laboratory

(Laboratory Temperature)

Storage period, days	IP upper pour pt, ° F	Storage period, days	IP upper pour pt, ° F	Storage period, days	IP upper pour pt, ° F
As prepared	Fluid at 0° F	7	−5	15	—
1	—	8	0	16	+10
2	10	9	−5	17	0
3	−15	10	−15	18	+20
4	−15	11	−5	19	+15
5	0	12	−10	20	+10
6	+5	13	−5	21	+15
		14	+30		

TABLE XII

"As Received" and IP Upper Pour Point Behaviour of a Fuel Oil Stored in a Refinery Laboratory

(Laboratory temperatures)

Storage period, days	Pour point, ° C		Storage period, days	Pour point, ° C	
	"As received"	IP upper pour pt		"As received"	IP upper pour pt
As prepared	−3	18	23	+9	21
1	−3	18	24	+9	21
2	−3	18	25	+9	21
3	−3	18	26	+9	21
4	0	18	27	+9	21
5	0	18	28	+9	21
6	0	18	29	+9	21
7	0	18	30	+9	21
8	0	18	31	+9	21
9	0	18	32	+9	21
10	0	18	33	+9	21
11	+3	21	34	+9	21
12	+3	21	35	+9	21
13	+3	21	36	+12	21
14	+3	21	37	+12	21
15	+3	21	38	+12	21
16	+6	21	39	+12	21
17	+6	21	40	+12	21
18	+6	21	41	+12	21
19	+6	21	42	+12	21
20	+9	21	43	+12	21
21	+9	21	44	+15	21
22	+9	21	45–58	+15	21

Other instances were reported by individual members in which significant increases in IP upper pour point had been experienced either in bulk storage (land installations or during bulk shipment) or in laboratory stored samples, and Table XIII gives the results obtained by a member in an attempt to find out whether pour point changes recorded on small samples of a fuel oil were reproduced in larger amounts of fuel.

For this work, a freshly prepared fuel oil, made by blending in the laboratory from fresh refinery components, was stored: (*a*) in pour point jars; (*b*) in 5-gallon drums. Pour point jar storage was effected at 32° F, laboratory temperature and ambient outside temperature; 5-gallon drum storage was effected at laboratory temperature. Sufficient samples were laid down to permit observations to be made in duplicate.

TABLE XIII

The Pour Point Behaviour of a Freshly Prepared Fuel Oil Stored at 32° F, Laboratory Temperature and Outside Temperature

Days of storage / Storage conditions	IP upper pour point, ° F						" As received " pour point, ° F					
	32° F	Laboratory temp		Outside temp			32° F	Laboratory temp		Outside temp		
	Pour pt jars	Pour pt jars	5-gal drum	Pour pt jars			Pour pt jars	Pour pt jars	5-gal drum	Pour pt jars		
0	20 20	20 20	20 20	20 20			−5 0	−5 0	−5 0	−5 0		
1	30	25		20			0	0		0		
2	20	20		20			5	5		5		
5	15	15		15			5	5		5		
7	25	25		30			5	10		5		
9	30	45		30			10	10		10		
12	25	30		30			10	10		20		
14	20	25		25			20	20		15		
16	30	35		30			—	—		—		
19	30	35		30			5	5		5		
21	20	25		20			5	5		10		
27	30	25		25			10	15		10		
29	35	35		35			10	15		20		
33	35	35		35			25	15		15		
40	30	40		35			15	5		10		
47	35	45		45			10	10		10		
54	20	40		35			10	20		10		
77	35	35		40			45	30		35		
83	30	45		35			10	30		35		
84	25 30	40		35			15 20	25		30		
85	30 35	45 45		40			15 20	15 20		45		
90	35	45 45		45			20 —	20 30		45		
98	— —	— —	40 45	45	50		— —	— —	35 40	45	50	
Mean final value	30	45	45	45			20	25	40	45		

The results given in Table XIII are summarized in Table XIV.

Thus all samples showed a definite increase in both IP upper pour point and " as received " pour point with age at the storage temperatures employed. The rise in the case of the samples stored in pour point jars was erratic, but no evidence as to the regularity of the rise was obtained for the 5-gallon samples, since these were left undisturbed until their final pour points were determined.

The erratic pour points encountered in this and earlier work (Table XI) were first thought to be a laboratory phenomenon. However, repeat experiments confirmed that these fuels gave erratic pour points, and similar behaviour was also observed in other fuels, both in laboratory and bulk storage.

To investigate the possibility that vibrations in the laboratory could affect the repeatability of pour point determinations, a pour point sensitive fuel was subjected to frequent tilting of the pour point jar, to vibrations of short wavelength and low amplitude, and to vibrations of long wavelength and high amplitude, but none of these factors induced any change in the pour point of the fuel.

TABLE XIV

Pour Point Behaviour of Freshly Prepared Fuel Oil

Storage conditions	Storage temperature	IP upper pour point behaviour
Pour point jar	32° F	Erratic rise from 20° to 30° F
Pour point jar	Room	Erratic rise from 20° to 45° F
Pour point jar	Outside	Erratic rise from 20° to 45° F
5-gal drum	Room	Rise from 20° to 45° F
		" As received " pour point behaviour
Pour point jar	32° F	Erratic rise from −5° to 20° F
Pour point jar	Room	Erratic rise from −5° to 25° F
Pour point jar	Outside	Erratic rise from −5° to 45° F
5-gal drum	Room	Rise from −5° to 40° F

These facts required recognition of the erratic pour point as a form of pour point instability, although no explanation of the phenomenon is apparent.

The foregoing examples, together with the many other instances of both commercial and laboratory storage experiments reported by members, was taken by the Panel as constituting substantial evidence that the IP upper pour point of a freshly prepared fuel oil could increase significantly with age. It was consequently agreed that in such cases the thermal pretreatment prescribed in the IP upper pour point method was unsuitable for the Panel's purposes.

It was accordingly decided to investigate the phenomenon of change in IP upper pour point with age, paying particular attention to:

(*a*) Its nature and magnitude.
(*b*) Its frequency of occurrence.

CHANGE IN IP UPPER POUR POINT WITH AGE

It was agreed to investigate the changes in IP upper pour point with age of freshly prepared fuel oils in both bulk storage and laboratory storage. This necessarily involved the co-operation of refineries or installations, and difficulties were envisaged in arranging for samples of freshly prepared fuel oils to be made available to Panel members for examination. These difficulties arose primarily from the delay inevitable in transporting a suitable quantity of freshly prepared fuel oil from the refinery or installation to Panel members, for it was considered essential that observations should be made on the fuel within 24 hours of its preparation.

It was also decided to see whether it was possible to bring an aged fuel back to its freshly prepared condition by means of a laboratory procedure and to attempt the preparation of a fuel oil both by careful distillation of crude petroleum and by blending up components obtained with the minimum possible delay from a refinery.

ATTEMPTED REGENERATION OF FRESHLY PREPARED CONDITION OF AN AGED FUEL OIL

Several members advised that heating a naturally aged fuel oil to a temperature above that of its IP upper pour point would be likely to bring it to a condition approximating to its freshly prepared ("birth") condition. Accordingly, in one series of experiments, samples of the fuel oil (Table XIII) which had been stored (after preparation) for 98 days at room temperature in a 5-gallon drum were heated to various temperatures and maintained at these temperatures for 2 hours. The samples were then allowed to cool overnight, whereafter their pour points were determined.

TABLE XV

Effect of Heat Treatments on the Pour Points of an Aged Fuel Oil

Storage, days	Preliminary heat treatment, ° F	Pour point, ° F		Viscosity sec Red I at 122° F
		IP upper	"As received"	
0	—	20, 20	−5, 0	369
98	—	40, 45	35, 40	360
98	100	40, 40	35, 40	360
98	210	30, 30	5, 5	390
98	300	10, 15	0, 0	450

This fuel was considered to be particularly useful for these experiments in view of the significant increase in both IP upper pour point and "as received" pour point during its 98 days' storage.

TABLE XVI

Effect of Heat Treatment at 300° F, with Precautions to Prevent Viscosity Increases, on the Pour Points of an Aged Fuel Oil

	Blank 98 days room temp storage	Sample heated for 3 hours, under reflux	
		In air	In nitrogen
Viscosity, sec Red I at 122° F	343, 342	352, 356	347, 347
IP upper pour pt, ° F	+40, +40	+10, +5	+5, +5
"As received" pour pt, ° F	+30, +30	+5, +5	−5, −5

It will be noted from Table XV that:

(i) Heating at 300° F restores both the IP upper pour point and the "as received" pour point to values close to those recorded immediately after blending.

(ii) Heating at 100° F has little effect on the IP upper pour point and "as received" pour point measured after 98 days' storage.

(iii) At 300° F heat treatment, the Redwood viscosity at 122° F increases.

It appeared from these experiments that the pour point of the freshly prepared fuel could be reached again by the heat treatment but that the viscosity increased as a result of the treatment. This viscosity increase was further investigated by taking a sample which had been stored for 98 days at room temperature and heating it for 3 hours under reflux in air in one case and under nitrogen in another. Viscosity and pour point determinations were then made and are given in Table XVI. These results suggested that the increase in viscosity observed in the first experiments (*cf* Table XV) was entirely due to loss of volatile material from the sample.

Similar experiments to those recorded in Table XV

were made by other members with various fuel oils, but the results were found to conflict. In one case it was found that at the end of the heat treatment at 300° F, the pour point returned to that of the " birth " condition of the fuel and then proceeded to increase again with age. This was the kind of results sought by the Panel, but other members reported that either the fuels they investigated did not age after heat treatment, or that heating to some temperature such as 300° F was in itself insufficient to regenerate the " birth " condition of the fuel.

It was concluded that an aged fuel oil could not in general be returned to its " birth " condition by means of laboratory heat treatment.

PREPARATION OF FRESHLY PREPARED FUEL OIL BY LABORATORY DISTILLATION

The feasibility of preparing in the laboratory a fuel oil which would subsequently show an aging effect was investigated by a member as follows.

A crude petroleum was topped to 300° C and the bottoms fractionated in a Hickman molecular still, the entire operation being conducted in a manner which precluded the possibility of cracking. The fractions were then blended with the bitumen residue in the proportions in which all were present in the original crude to give a fuel oil of viscosity 380 sec Redwood I at 122° F. Portions of this fuel were stored in pour point jars at 50° F and 80° F, pour point determinations being made on these samples at suitable intervals.

In another experiment the distillation was made in such a way as to permit considerable cracking to occur during the preparation of the fraction from which the oil was blended. For this preparation, the crude petroleum was topped to 300° C in a distillation flask and the distillate redistilled in a packed column equivalent to 10 to 15 theoretical plates, the cut boiling above 250° C being called " light gas oil." The residue from the initial distillation boiling above 300° C was then distilled in a small stainless steel pot still to a final temperature of 400° C at 99 mm Hg (equivalent to 500° C at atmospheric pressure). The fraction 300°–500° C was called " waxy distillate " and the residue boiling above 500° C " bitumen." This bitumen was then heated to 300° F and the light gas oil, previously heated to 300° F, mixed with it; the whole was allowed to cool at 120° F and the waxy distillate, previously heated to 120° F, added to it. The fuel oil thus blended was then allowed to cool to about 80° F before being placed in pour point jars for storage at 50° F and 80° F.

The behaviour on storage of the fuels prepared by the two methods of distillation is compared in Tables XVII and XVIII.

TABLE XVII

Storage of Laboratory Prepared Fuel Oils at 50° F

Age of sample, days	Uncracked oil		Cracked oil	
	" As received " pour pt, ° F	IP upper pour pt, ° F	" As received " pour pt, ° F	IP upper pour pt, ° F
On preparation	−5	5	−5	15
1	0	10	0	0
2	0	15	5	10
3	0	—	0	15
4	—	—	0	5
7	0	20	10	10
14	0	20	10	15
22	0	20	25	15

TABLE XVIII

Storage of Laboratory Prepared Fuel Oils at 80° F

Age of sample, days	Uncracked oil		Cracked oil	
	" As received " pour pt, ° F	IP upper pour pt, ° F	" As received " pour pt, ° F	IP upper pour pt, ° F
On preparation	−5	5	−5	15
1	−5	—	0	−5
2	−5	25	−5	0
3	−5	25	−10	−5
4	0	—	−10	−5
7	0	40	0	15
14	0	30	−5	15
22	0	30	−5	15

It will be seen that for storage at 50° F:

(i) The " as received " pour point of the uncracked oil showed no significant change over a period of 22 days, whereas this pour point for the cracked oil increased significantly after a few days;

(ii) The IP upper pour point for the uncracked oil increased from 5° to 20° F within a period of seven days, remaining stationary thereafter. The IP upper pour point of the cracked oil showed no significant change throughout the testing period.

For storage at 80° F, however:

(i) The " as received " pour point of the uncracked oil showed no significant change over the test period and this pour point behaved similarly for the cracked oil after showing some fluctuation in the first few days following its manufacture;

(ii) The IP upper pour point for the uncracked oil showed a net increase of 25° F over a period of 22 days. The IP upper pour point of the cracked oil remained sensibly constant after showing some fluctuation in the first few days of its life.

These results are summarized in Table XIX and show that the only evidence of an aging effect is given by the IP upper pour point at both storage temperatures for the uncracked oil and by the "as received" pour point at 50° F storage temperature only for the cracked oil.

TABLE XIX

Fuel / Storage temp	Behaviour of pour point, °F			
	50° F		80° F	
	"As received" pour point	IP upper pour point	"As received" pour point	IP upper pour point
Uncracked	Stationary	Increased	Stationary	Increased
Cracked	Increased	Stationary	Stationary	Stationary

It was concluded that the experiment of recombining laboratory distillate fractions was only partially successful in providing a means of preparing a fuel oil in the laboratory which would simulate the pour point aging behaviour of a fuel produced in practice.

PREPARATION OF A FRESHLY PREPARED FUEL OIL USING REFINERY SUPPLIED COMPONENTS

As an alternative to the purely laboratory preparation of a fresh fuel oil, either by a regenerative procedure or from crude petroleum, arrangements were made with a U.K. refinery for the supply in fresh condition of the components used in a grade of fuel oil believed at the time to be exhibiting a pour point aging effect, together with a sample of the fuel itself. To this end, the refinery was visited, the fuel and its components transported immediately to the member's laboratory, and blending started with the minimum of delay.

TABLE XX

Storage Tests on Freshly Prepared Fuel Oil—Comparison of Laboratory Storage with Refinery Storage

Results from member's laboratory							Results from refinery									
Temperature of storage			Laboratory temperature				—				Laboratory temperature				Air temperature	
Conditions of storage			In 2-gal can		In pour point jars		—				In 2-gal can		In pour point jars		5000 tons in storage	
Age of sample,	Lab temp, °F		Pour point, °F		Pour point, °F		Lab temp, °F		Air temp, °F		Pour point, °F		Pour point, °F		Pour point, °F	
days	Max	Min	AR	IP	AR	IP	Max	Min	Max	Min	AR	IP	AR	IP	AR	IP
3	72	66	25	35	25	35	—	—	56	42	25	30	25	30	20	25
4	—	—	30	35	—	—	69	49	52	44	30	30	35	30	20	20
5	71	59	30	40	30	35	—	—	—	—	—	—	—	—	—	—
7	—	—	—	—	—	—	69	58	51	—	30	30	35	35	25	25
8	66	57	35	35	35	35	76	58	48	40	30	30	35	30	20	30
9	—	—	—	—	—	—	70	59	54	48	30	35	35	35	20	30
10	—	—	—	—	—	—	72	64	56	52	35	30	35	35	20	30
11	—	—	35	35	35	40	75	69	68	58	25	30	30	35	10*	30
14	—	—	—	—	—	—	77	63	64	46	15	35	35	40	15	35
15	67	63	35	35	30	35	77	66	62	56	30	35	30	40	15*	35
16	68	64	—	—	—	—	77	66	61	49	40	40	40	50	15	35
17	—	—	30	35	35	40	78	66	74	58	35	35	40	40	15	30
18	68	62	—	—	—	—	82	68	72	53	35	30	40	40	15	30
19	71	66	—	—	—	—	—	—	—	—	—	—	—	—	—	—
22	—	—	—	—	—	—	86	66	76	62	30	35	40	40	—	—
23	72	68	25	40	20	35	—	—	—	—	—	—	—	—		
24	74	68	—	—	25	—	—	—	—	—	—	—	—	—		
25	71	60	35	—	35	—	—	—	—	—	—	—	—	—		
26	—	—	30	35	30	35	—	—	—	—	—	—	—	—		
29	72	63	35	40	35	40	—	—	—	—	—	—	—	—		
31	70	62	—	—	35	40	—	—	—	—	—	—	—	—		
32	68	60	—	—	—	—	—	—	—	—	—	—	—	—		
41	74	67	—	—	—	45	—	—	—	—	—	—	—	—		
43	69	64	35	40	35	—	—	—	—	—	—	—	—	—		

Note: AR = "As received" pour point; IP = IP upper pour point.
* Small deliveries made from the tank between these dates.

The components involved comprised:

	% wt	IP upper pour point
Residue (*a*)	54·1	70
Residue (*b*)	4·4	25
Heavy gas oil	14·4	50
Light gas oil	24·6	−5
Cutter stock	2·5	−20
	100·0	

At the refinery the fuel blending (Blend A) was carried out by jet mixing in a 5000-ton tank. The residue (*a*) left the still at about 300° C (570° F), and was cooled to 160° F by the time it reached the mixing jet.

The plan agreed upon was as follows:

At refinery:

(i) Bulk storage of the fuel in unheated refinery tanks.

(ii) Small-scale storage of samples of this fuel in 2-gallon cans and pour point tubes at laboratory temperature.

TABLE XXI

Pour Points of Blends Stored in Pour Point Jars at Laboratory Temperature

Age of blend, days	"As received" pour point, ° F			IP upper pour point, ° F		
	Blend A	Blend B	Blend C	Blend A	Blend B	Blend C
Nil	—	40	50	—	40	50
1	—	45	50	—	40	50
2	—	45	50	—	—	50
3	25	—	—	35	—	—
4	—	45	—	—	45	—
5	30	40	50	35	—	50
7	—	40	50	—	50	50
8	35	—	—	35	—	—
9	—	40	—	—	—	—
11	35	—	—	40	—	—
12	—	40	—	—	45	—
13	—	—	50	—	—	50
14	—	35	—	—	50	—
15	30	—	—	35	—	—
17	35	—	—	40	—	—
20	—	35	—	—	50	50
21	—	—	45	—	—	—
23	20	—	—	35	—	—
24	25	—	—	—	—	—
25	35	40	—	—	45	50
26	30	—	50	35	—	—
28	—	40	—	—	50	—
29	35	—	—	40	—	—
31	35	—	—	40	—	—
33	—	—	50	—	—	—
37	—	—	—	—	—	50
40	—	40	—	—	55	—
41	—	—	—	45	—	—
43	35	—	—	—	—	—
45	—	—	—	—	—	—
50	—	—	50	—	—	55
55	—	—	—	—	—	60

At member's laboratory:

(i) Storage of the refinery-made fuel at laboratory temperatures in 2-gallon cans and pour point tubes.

(ii) Preparation of the fuel from its components using the same temperature conditions and order of mixing as those applying in the refinery blending procedure, followed by storage at laboratory temperatures in 2-gallon cans and pour point tubes.

The results of the tests made in the member's laboratory and at the refinery on the finished fuel are set out in detail in Table XX. These results indicate that there is no marked increase of pour point with age during the storage period with this particular fuel.

In accordance with the original plan, the laboratory blends were prepared from the refinery components,

TABLE XXII

Pour Points of Blends Stored in Pour Point Jars at 80° F

Age of blend, days	"As received" pour point, ° F			IP upper pour point, ° F		
	Blend A	Blend B	Blend C	Blend A	Blend B	Blend C
Nil	—	40	50	—	40	50
1	—	40	45	—	45	50
2	—	40	45	—	—	50
3	25	—	—	35	—	—
4	—	25	—	—	50	—
5	25	30	45	35	50	50
7	—	30	45	—	55	50
8	30	—	—	50	—	—
9	—	30	—	—	—	—
11	25	—	—	50	—	—
12	—	25	—	—	50	—
13	—	—	40	—	—	50
14	—	30	—	—	55	—
15	30	—	—	50	—	—
17	30	—	—	—	—	—
20	—	20	—	—	50	—
21	—	25	40	—	—	50
23	30	—	—	50	—	—
25	—	35	—	45	50	50
27	—	40	40	—	—	—
28	35	35	—	—	50	—
30	—	35	—	—	—	—
31	35	—	—	—	—	—
33	—	30	50	—	—	—
38	—	—	50	55	—	55
40	—	40	—	—	—	—
43	30	—	—	—	—	—
45	—	35	—	—	55	—
50	—	—	50	—	—	55
55	—	—	50	55	—	55
58	30	—	—	55	—	—
63	35	—	—	—	—	—
65	—	—	50	55	—	55
70	—	—	50	—	—	—

two procedures being adopted, namely: Blend B, in which residue (*a*) was heated to 160° F before blending it with the other components, and Blend C, in which residue (*a*) was heated to 570° F and then allowed to cool slowly to 160° F before blending.

Tables XXI–XXIII give the results of the laboratory storage in pour point jars of the original refinery fuel (designated Blend A), and the two laboratory blends B and C, at laboratory temperature, 80° F

and 50° F respectively. These results may be summarized as follows:

(*a*) The pour points of the three blends are different, Blend A giving in general the lowest and Blend C the highest.

(*b*) The pour point of Blend A tended to show the largest increase and that of Blend C the least increase, while that of B was intermedial.

It was therefore considered that variations in blending procedure have an important effect on the pour point. The importance of precise control of the blending procedure is illustrated by the results given in Table XXIV for a two-component blend. A blend of 69 per cent wt residue (*a*) and 31 per cent wt light gas oil (two of the components of Blend A) was made up a number of times under conditions in which the blending temperatures of both components were varied. The "as received" pour points of these blends varied between 10° and 45° F. Hence it was further concluded that considerably more must be known about the effects of variation in blending procedure on pour point before laboratory-prepared blends can be expected to duplicate the pour point behaviour of blends prepared in bulk. Such information might prove valuable to the refinery in enabling them to choose blending conditions most likely to lead to stable pour point behaviour in the finished fuel.

TABLE XXIII

Pour Points of Blends Stored in Pour Point Jars at 50° F

Age of blend, days	"As received" pour point, °F			IP upper pour point, °F		
	Blend A	Blend B	Blend C	Blend A	Blend B	Blend C
Nil	—	40	50	—	40	—
1	—	35	50	—	35	50
2	—	25	50	—	—	50
3	25	—	—	35	—	—
4	—	30	—	—	40	—
5	35	30	45	40	—	50
7	—	30	50	—	35	50
8	35	—	—	50	—	—
9	—	30	—	—	—	—
11	35	—	—	40	—	—
12	—	35	—	—	35	—
13	—	—	50	—	—	50
14	—	30	—	—	40	—
15	35	—	—	40	—	—
17	35	—	—	45	—	—
20	—	30	50	—	40	50
23	40	—	—	45	—	—
25	—	30	—	—	35	—
26	—	—	50	—	—	50
28	—	30	—	—	40	—
29	35	—	—	40	—	—
33	—	—	50	—	—	—
37	—	—	—	—	—	50
39	—	35	—	—	40	—
40	—	—	—	—	—	—
42	—	—	—	—	—	—
43	45	—	—	40	—	—
45	40	—	—	—	—	—
46	—	35	—	—	40	—
50	—	—	50	—	—	50
55	—	—	50	—	—	50
58	45	—	—	45	—	—
60	—	—	—	—	40	—
63	35	—	—	50	—	—
65	—	—	50	—	—	55
70	—	—	—	—	—	—
73	30	—	—	50	—	—

TABLE XXIV

Blends of Residue (a) and Light Gas Oil

Blend	Temp to which residue (*a*) heated before blending, °F	Temp of residue (*a*) on blending, °F	Temp of light gas oil on blending, °F	Temp after mixing of residue (*a*) and light gas oil, °F	"As received" pour pt, °F
1	160	160	160	160	15
2	160	160	75	136	25
3	160	160	40	130	15
4	160	140	140	140	25
5	160	140	75	122	15
6	160	140	40	112	10
7	160	130	130	130	40
8	160	130	75	114	35
9	160	130	40	108	35
10	160	120	120	120	40
11	160	120	75	105	25
12	160	120	40	100	45

Composition of Blends

Component	% by weight
Residue (*a*) . . .	69
Light gas oil . . .	31

DISCUSSION

Data obtained on a large number of different fuel oils in representative commercial storage showed that the "as received" pour point was rarely as high as the IP upper pour point, although the two values were often close together. It seemed, therefore, that the heat treatment of the IP upper pour point provided a suitable means of inducing in a sample of oil the condition which was likely to be reached by the same oil in typical commercial storage. This conclusion was based, however, on values of the IP upper pour point and the "as received" pour point determined on a sample taken after the oil had been in storage for some time, and further work of the Panel showed that the IP upper pour point could often change significantly during the first few days or weeks after the oil was blended. It followed that the effect of the heat treatment used in the IP upper pour point method could vary with the age of the oil and, in particular, it could not be relied upon to induce in a freshly blended oil the condition which is likely to be reached after normal commercial storage.

The Panel took the view that the test under development required a method of conditioning which was independent of the age of the oil and, with the object of finding such a method, attention was directed to the investigation of the changes in pour point with age.

The possibility of regenerating the " birth " condition of an aged oil by heating it to temperatures as high as 300° F was investigated in the hope that this would provide a convenient laboratory means of obtaining samples with the characteristics of freshly blended oils. It was found, however, that although with some oils the original IP upper pour point could be regenerated, the subsequent behaviour of the regenerated oil was not the same as that of the original oil. Investigations were then made with laboratory blends prepared either from fresh refinery components or from components obtained by the laboratory distillation of crude oil. It appeared from this work that the actual pour point and the subsequent changes in pour point with age depended on the temperature of blending and the order in which the components were mixed. For these reasons it was difficult to reproduce in the laboratory blends the behaviour of blends prepared at the refinery from the same components. It was decided at this stage that a report reviewing the situation should be prepared before proceeding with any further experimental work.

It should be noted that the case in which the IP upper pour point increases with the age of the oil presents a real difficulty in the present situation only if this change in pour point is reflected in an appreciable change in the temperature at which the oil becomes too viscous for economical pumping (24 poise). This has not yet been established, and it is suggested that any further work should start with tests in which freshly blended oils and the same oils after aging are subjected to the heat treatment of the IP upper pour point method and then examined in a coaxial rotating viscometer to determine the temperature at which the viscosity reaches a value of 24 poise at a rate of shear of about 13 sec^{-1} (corresponding with a shearing stress of about 300 dynes/cm^2). It has been shown by Panel F of AFLAC that the Ferranti instrument is a suitable viscometer for this purpose.

If further investigations should show that the mobility of the oil after the heat treatment of the IP upper pour point method does not vary appreciably with age, the adoption of this heat treatment in the proposed mobility test would be justified. If, on the other hand, the mobility was found to decrease appreciably with age for oils which showed an increase in IP upper pour point with age, some modification of the conditioning process would be necessary to obtain an assessment independent of the age of the oil. One possibility which might be tried in this case would be to use the reheat temperature (*cf* Fig 2), giving the highest pour point with a given oil in place of the standard temperature of 115° F.

ERRATA

Oil and Gas Segregation in Oilfield Reservoirs.

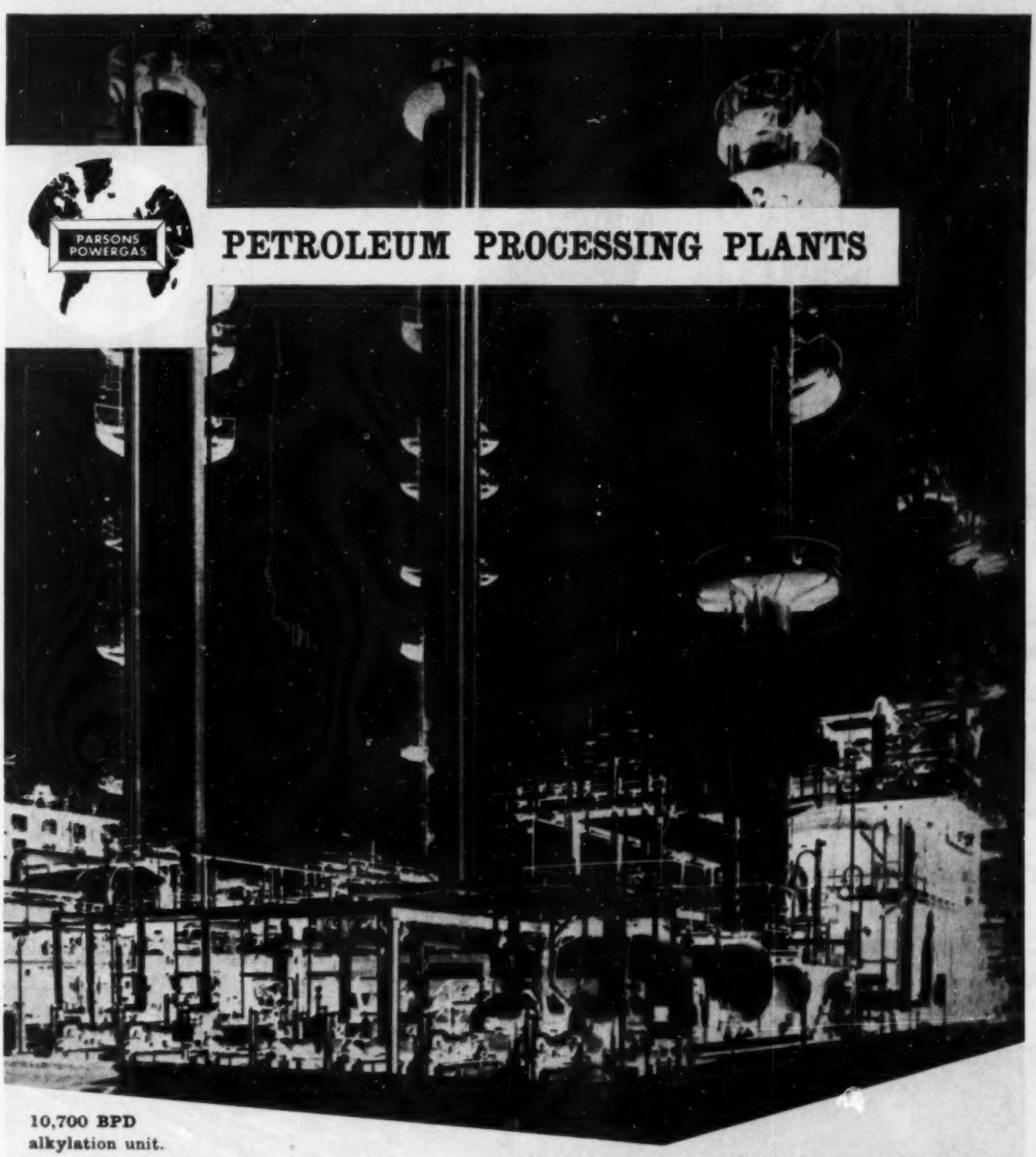
H. Gilmour. December 1960 *Journal*, pp. 383–390.

Fig 1, p 384, and Fig 5, p 387. The titles are correct but the diagrams have been transposed.

Page 386, left-hand column, 5th line. For "q_w" read "q_o".

Equation 4, p 387. The symbol, μ, has been omitted from the second term on the right-hand side. The correct equation is:

$$V_o = \frac{K_o}{\mu_o} l_g g - \frac{K_o}{\mu_o} \frac{dP_g}{dz} - \frac{K_o}{\mu_o} \frac{dP_c}{dz}$$



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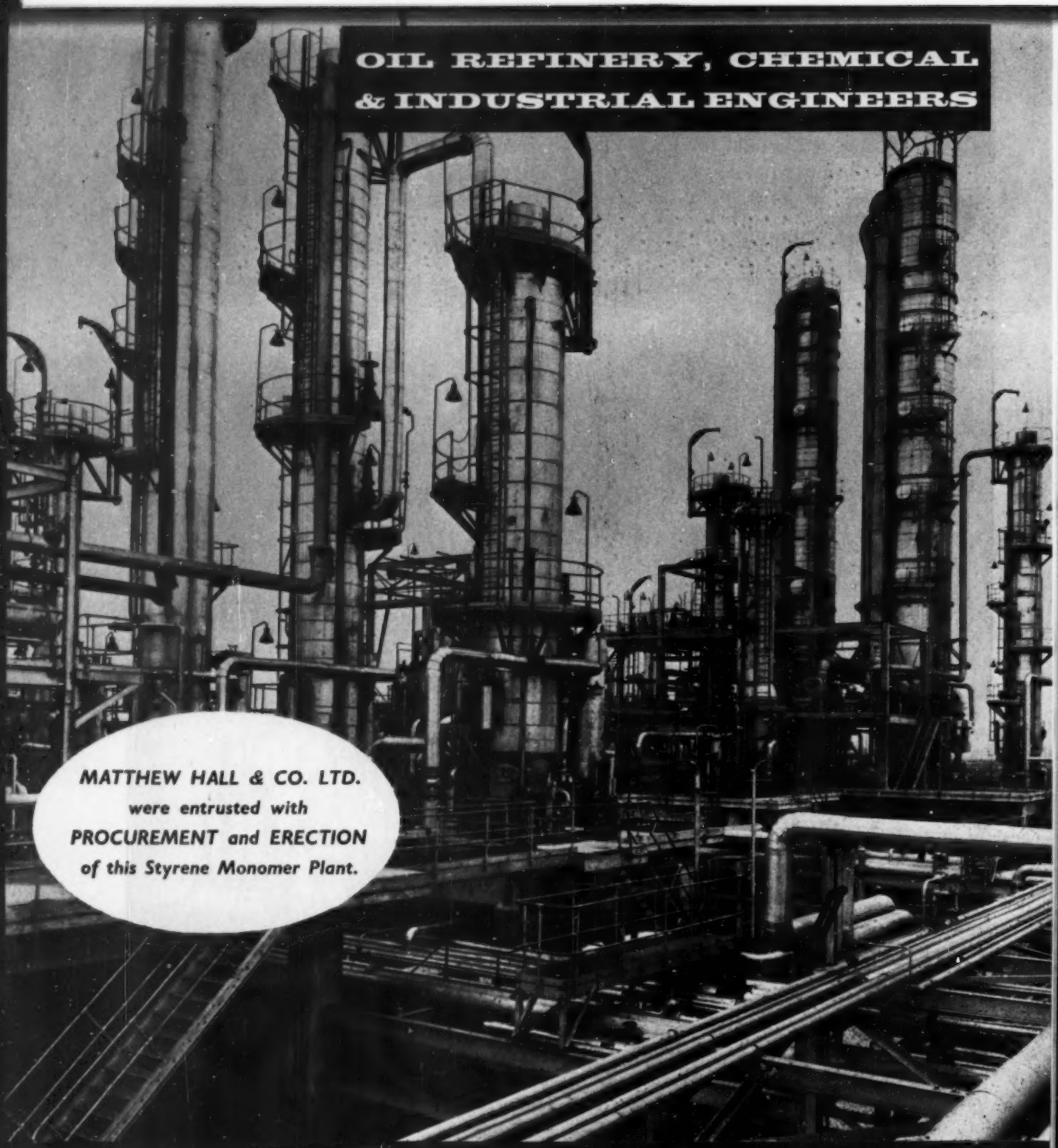

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Hose Exchange Room at Stanlow. (Shell Refining Co. Ltd.)

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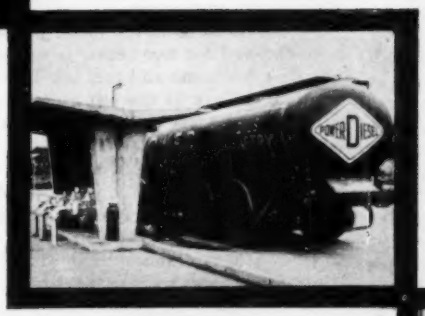
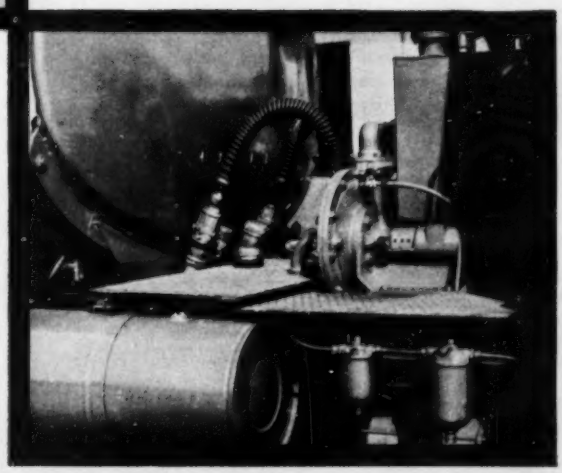


Bottom loading-truck, using 2½" Self-Sealing Couplings. (Power Petroleum Co. Ltd.)

1½" Self-Sealing Couplings in use on Vacuum Oil Company Tanks. (South Africa.)



Avery-Hardoll industrial couplings eliminate wasteful, dangerous spillage. Self-sealing valves prevent flow from starting until the Hose and Tank Units are fully coupled. On disengagement, the valves return to the self-sealing position before the Units are uncoupled. Avery-Hardoll industrial couplings are widely used for rapid, safe bulk-handling in breweries, aviation, and for food processing industries.

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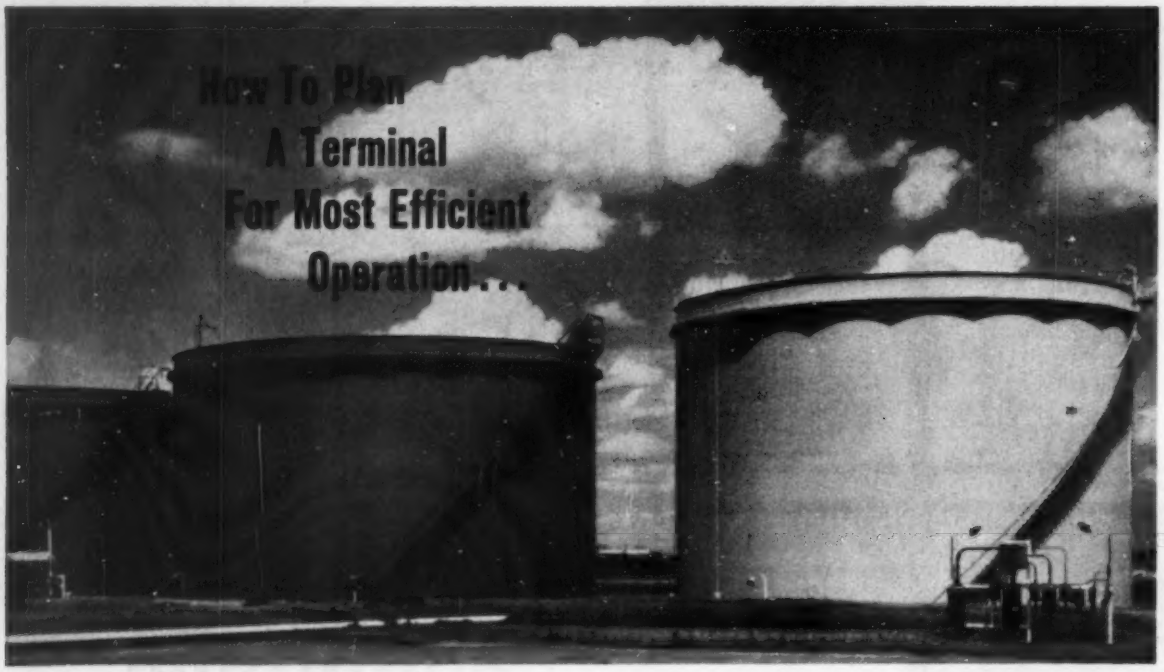

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The terminal in the upper photograph stores gasoline where pumping in and pumping out are almost daily procedures. For such operation, the owner wisely selected Graver Centerweighted Floating Roof Tanks to combat vapor losses during frequent fillings and emptyings.

In the terminal in the lower photograph, storage was planned for marketing a variety of products, gasoline, kerosene and fuel oil. The Graver Expansion Roof Tank at the left and the large cone roof tank preserve the volatility of stored gasoline during less frequent turnovers.

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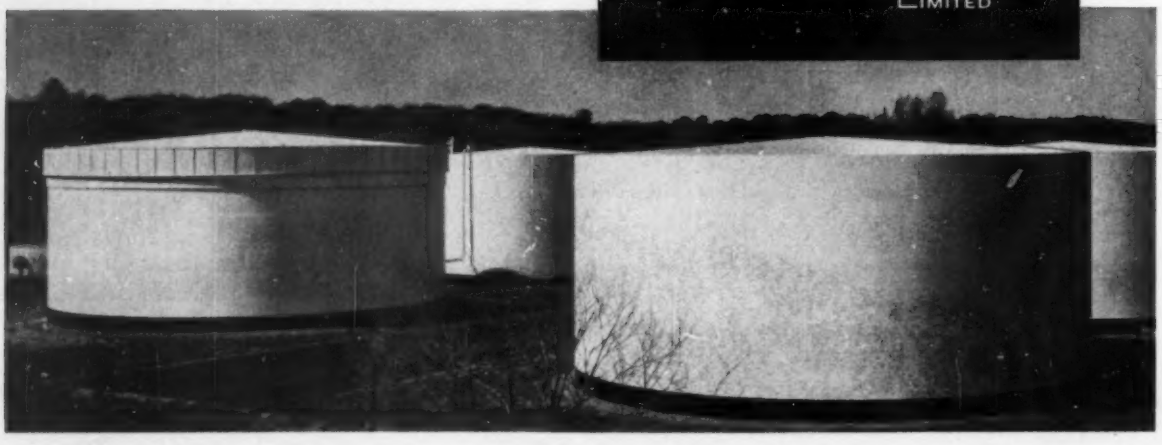

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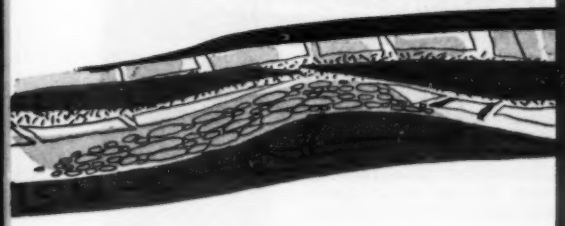

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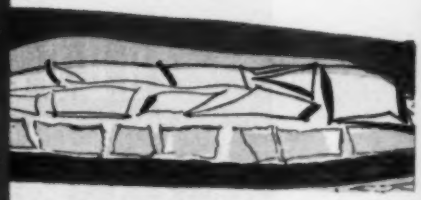

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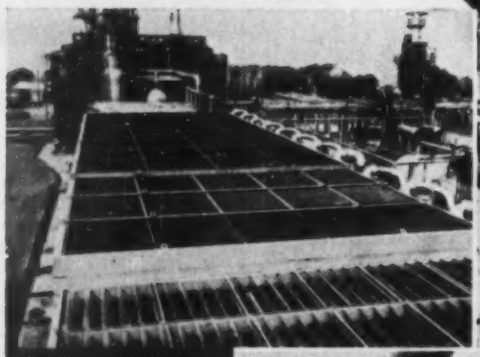

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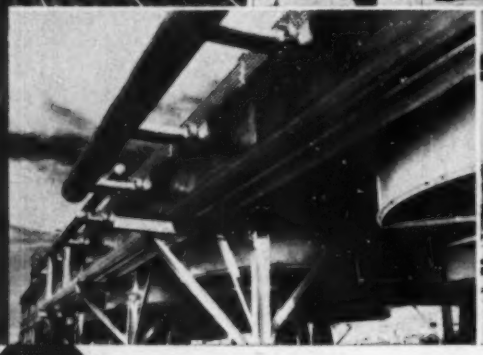

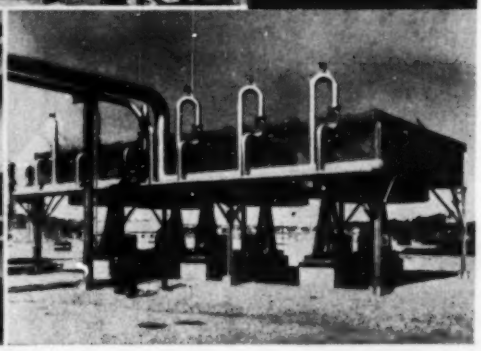

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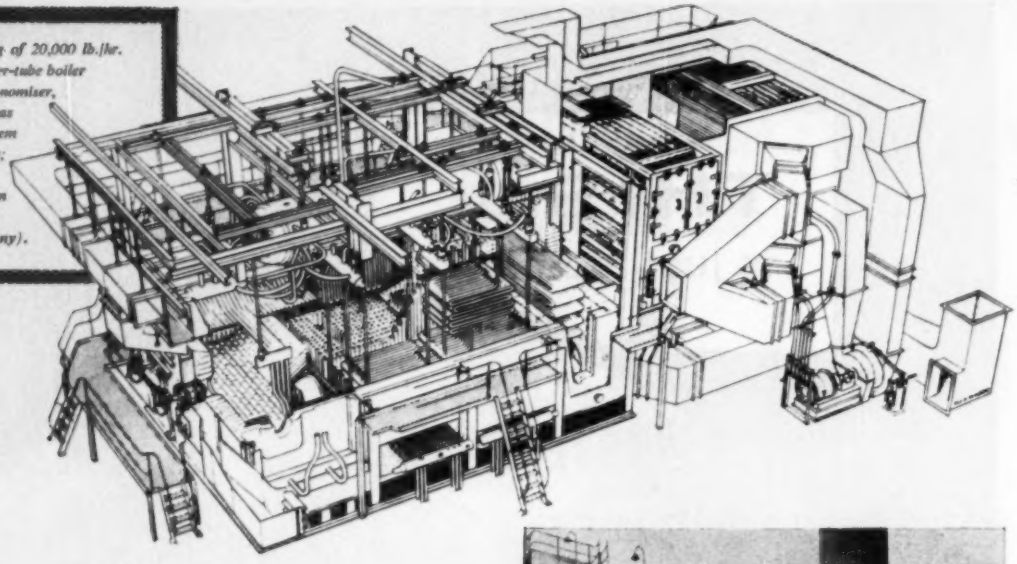


Cut-away drawing of 20,000 lb./hr. experimental water-tube boiler equipped with economiser, air-heaters, flue-gas re-circulation system and other features; for full-scale, fuel-oil combustion research (British Petroleum Company).

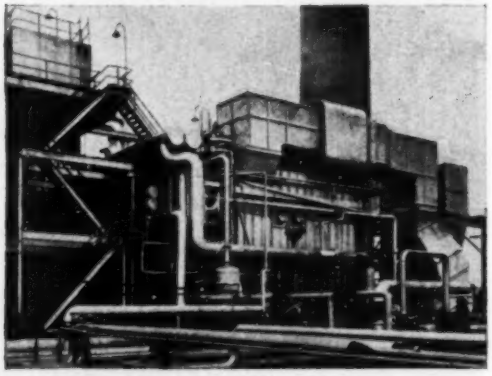
Tailor-made or "off-the-peg"

The special experimental boiler shown above has been designed and built by Babcock to British Petroleum Company specifications, for research—at a new B.P. combustion laboratory—into the methods and effects of burning liquid fuels under full-scale operating conditions.

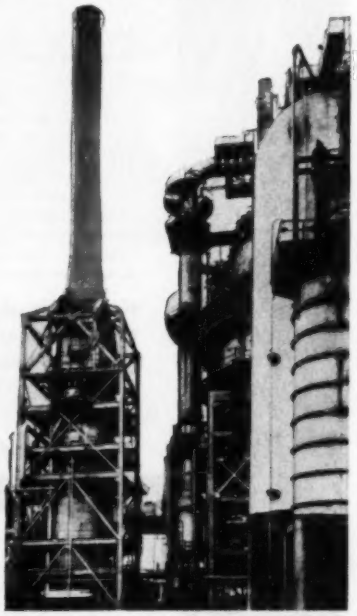
It was Babcock also that designed and built the special 300,000 lb./hr. CO boiler (below, right) at the Esso Fawley refinery, to utilize the steam-generating potential of the exhaust gases from a catalytic cracker.

In refineries and chemical plant the world over, conventional Babcock boilers of all types and sizes, fired with a wide variety of fuels and in both indoor and outdoor installations are, reliably and economically, supplying steam for heating, processing and power production.

So it is that Babcock is serving the oil and chemical industries with a wide range of plant—tailor-made to special requirements or built to established, "off-the-peg" Babcock designs.



Type FH oil-fired Integral Furnace boiler in an outdoor installation; (Esso refinery, Fawley).



300,000 lb./hr. CO boiler, operating on "waste" gases from a catalytic cracker; (Esso refinery Fawley).

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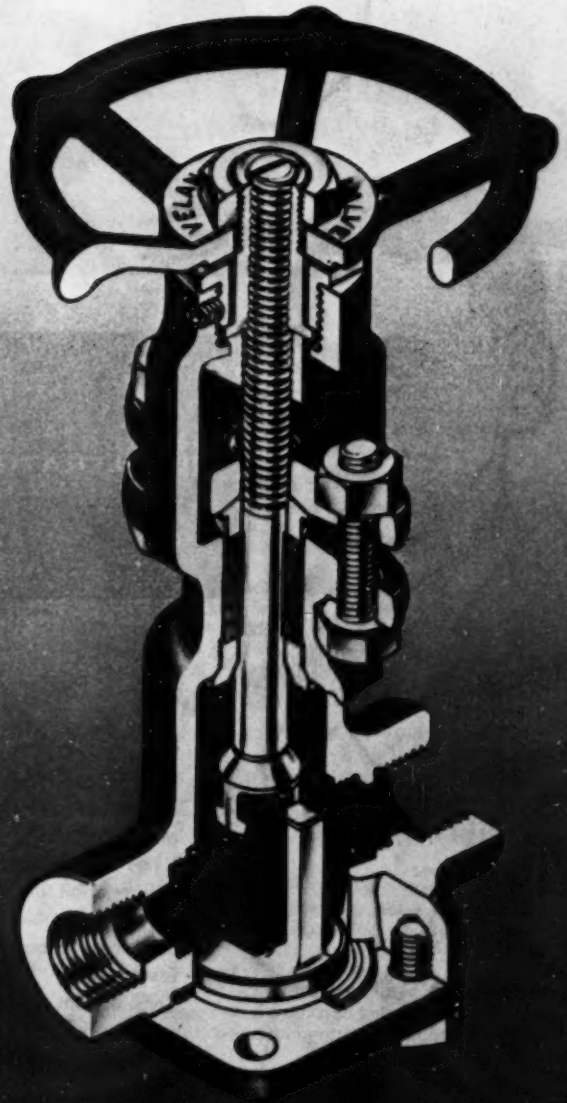

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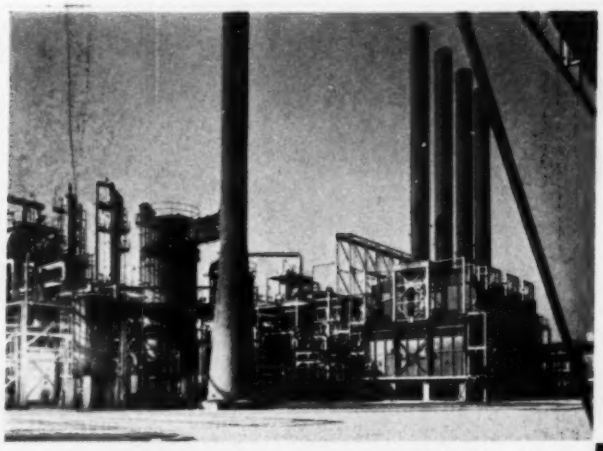
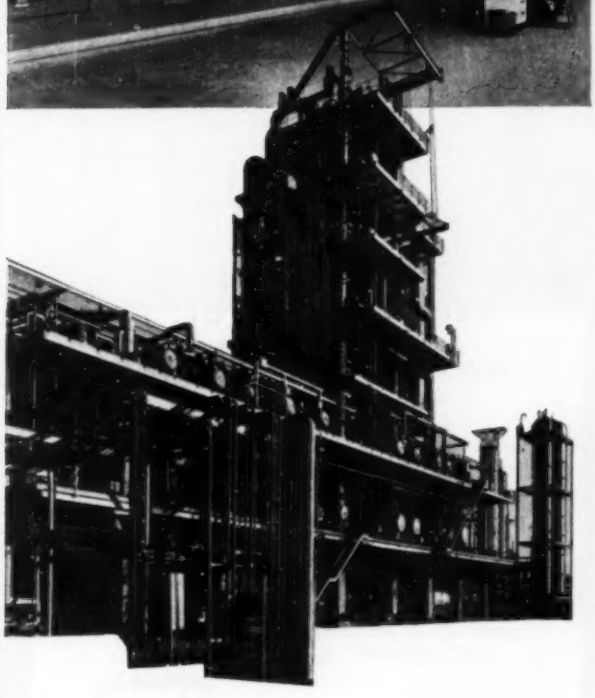


NEW SHELL CHEMICAL COMPANY ETHYLENE UNIT ON STREAM AT CARRINGTON, ENGLAND



The new Shell Chemical Company Ltd., Ethylene Unit, Carrington, England, has just been placed on stream. This unit was built for Shell by Kellogg International Corporation, London. It is designed ultimately to produce 55,000 long tons per annum of Ethylene from a straight run naphtha feed.

In addition to high purity Ethylene products, the unit produces debutanized gasoline, fuel oil, a Butadiene/Butylene product, with Propylene and Ethane, plus a refinery gas for fuel.

Naphtha is cracked in Kellogg steam cracking furnaces, using a very low steam to naphtha ratio for optimum yields at minimum operating costs. In order to increase the economy of operations, the effluent from the cracking furnaces is quenched and subsequently scrubbed with gas oil to remove entrained polymers and solids. Heat exchange is utilized to generate medium pressure steam. After separation of the heavy ends, the remaining gas is subjected to water and caustic wash, drying, and acetylene removal before passing to the low temperature separation section for recovery of Ethylene and other fractions.

Refrigeration is accomplished using Ethylene and Propylene as refrigerants, three temperature levels being used in each case, the lowest level being — 150°F. A further degree of cooling is obtained by utilization of the Joule-Thompson effect in the Demethanizer. An extensive heat exchange system is employed to keep the refrigeration load to a minimum and thus keep operating cost low.

The No. II Unit at Carrington is the first built for Shell by Kellogg International Corporation in the United Kingdom. Kellogg International Corporation supplied complete services covering all aspects of process design, engineering, procurement and construction, together with a team of operators for the commissioning programme.

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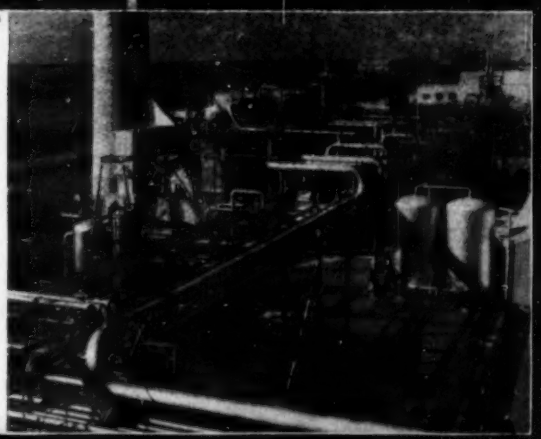

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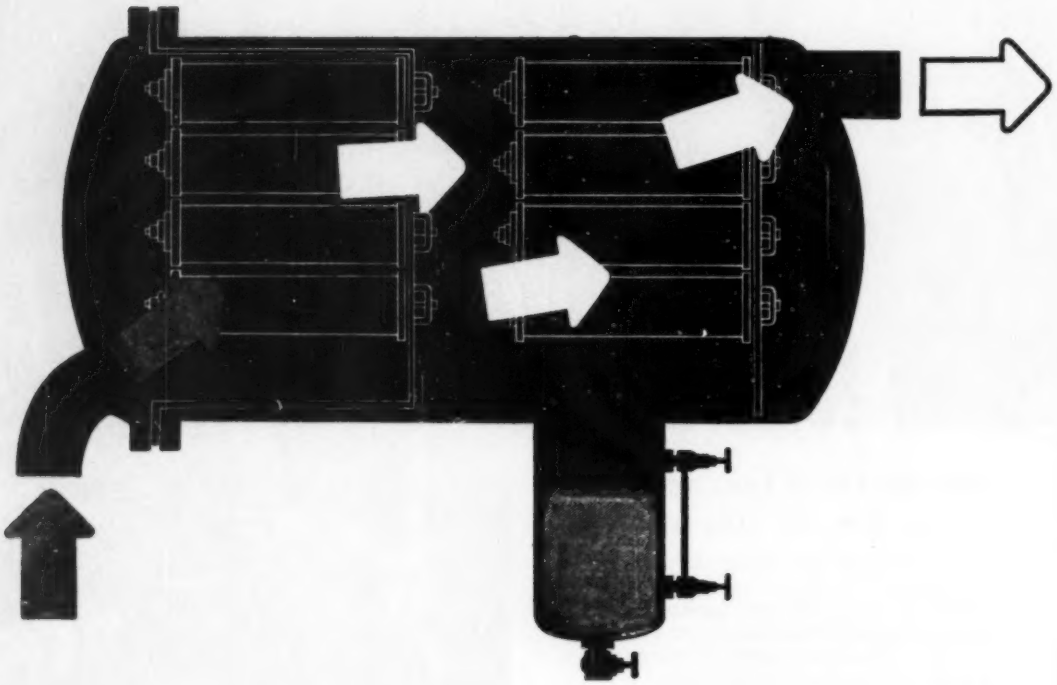

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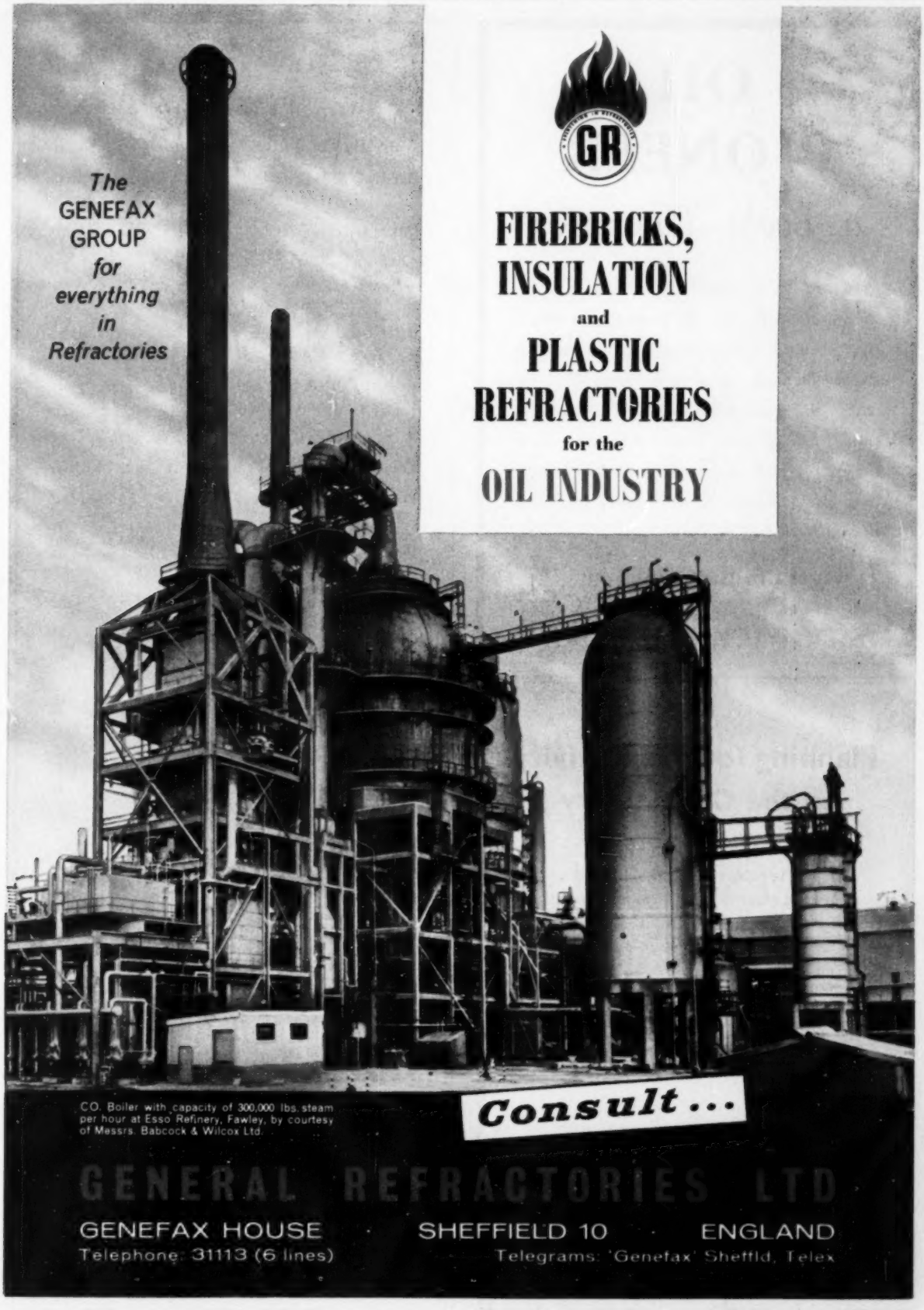
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